Chemistry

Part II

Textbook for Class XII

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12086

विद्यया ऽमृतमश्नुते

एन सी ई आर टी
NCERT

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FOREWORD

The National Curriculum Framework (NCF), 2005 recommends that children's life at school must be linked to their life outside the school. This principle marks a departure from the legacy of bookish learning which continues to shape our system and causes a gap between the school, home and community. The syllabi and textbooks developed on the basis of NCF signify an attempt to implement this basic idea. They also attempt to discourage rote learning and the maintenance of sharp boundaries between different subject areas. We hope these measures will take us significantly further in the direction of a child-centred system of education outlined in the National Policy on Education (1986).

The success of this effort depends on the steps that school principals and teachers will take to encourage children to reflect on their own learning and to pursue imaginative activities and questions. We must recognise that, given space, time and freedom, children generate new knowledge by engaging with the information passed on to them by adults. Treating the prescribed textbook as the sole basis of examination is one of the key reasons why other resources and sites of learning are ignored. Inculcating creativity and initiative is possible if we perceive and treat children as participants in learning, not as receivers of a fixed body of knowledge.

These aims imply considerable change in school routines and mode of functioning. Flexibility in the daily time-table is as necessary as rigour in implementing the annual calender so that the required number of teaching days are actually devoted to teaching. The methods used for teaching and evaluation will also determine how effective this textbook proves for making children's life at school a happy experience, rather than a source of stress or boredom. Syllabus designers have tried to address the problem of curricular burden by restructuring and reorienting knowledge at different stages with greater consideration for child psychology and the time available for teaching. The textbook attempts to enhance this endeavour by giving higher priority and space to opportunities for contemplation and wondering, discussion in small groups, and activities requiring hands-on experience.

The National Council of Educational Research and Training (NCERT) appreciates the hard work done by the textbook development committee responsible for this book. We wish to thank the Chairperson of the advisory group in science and mathematics, Professor J.V. Narlikar and the Chief Advisor for this book, Professor B. L. Khandelwal for guiding the work of this committee.

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Several teachers contributed to the development of this textbook; we are grateful to their principals for making this possible. We are indebted to the institutions and organisations which have generously permitted us to draw upon their resources, material and personnel. As an organisation committed to systemic reform and continuous improvement in the quality of its products, NCERT welcomes comments and suggestions which will enable us to undertake further revision and refinement.

Director
National Council of Educational
Research and Training

New Delhi
20 November 2006

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Rationalisation of Content in the Textbook

In view of the COVID-19 pandemic, it is imperative to reduce content load on students. The National Education Policy 2020, also emphasises reducing the content load and providing opportunities for experiential learning with creative mindset. In this background, the NCERT has undertaken the exercise to rationalise the textbooks across all classes. Learning Outcomes already developed by the NCERT across classes have been taken into consideration in this exercise.

Contents of the textbooks have been rationalised in view of the following:

- Overlapping with similar content included in other subject areas in the same class
- Similar content included in the lower or higher class in the same subject
- Difficulty level
- Content, which is easily accessible to students without much interventions from teachers and can be learned by children through self-learning or peer-learning
- Content, which is irrelevant in the present context

This present edition, is a reformatted version after carrying out the changes given above.

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THE CONSTITUTION OF INDIA

PREAMBLE

WE, THE PEOPLE OF INDIA, having solemnly resolved to constitute India into a [1]**[SOVEREIGN SOCIALIST SECULAR DEMOCRATIC REPUBLIC]** and to secure to all its citizens :

JUSTICE, social, economic and political;

LIBERTY of thought, expression, belief, faith and worship;

EQUALITY of status and of opportunity; and to promote among them all

FRATERNITY assuring the dignity of the individual and the [2][unity and integrity of the Nation];

IN OUR CONSTITUENT ASSEMBLY this twenty-sixth day of November, 1949 do **HEREBY ADOPT, ENACT AND GIVE TO OURSELVES THIS CONSTITUTION.**

---

1. Subs. by the Constitution (Forty-second Amendment) Act, 1976, Sec.2, for "Sovereign Democratic Republic" (w.e.f. 3.1.1977)
2. Subs. by the Constitution (Forty-second Amendment) Act, 1976, Sec.2, for "Unity of the Nation" (w.e.f. 3.1.1977)

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PREFACE

Chemistry has made a profound impact on the society. It is intimately linked to the well-being of human kind. The rate of advancements in chemistry is so high that curriculum developers continuously look for strategies to cope with these advancements. Also, the students have to be inspired to be the future leaders who would make fundamental contributions. The present textbook is a sincere effort in this direction.

The textbook, presented in two parts, comprises of sixteen Units. Although the titles of various Units indicate a sort of compartmentalisation into physical, inorganic and organic chemistry, readers will find that these sub-disciplines have been intermingled, at least to a certain extent, to have a unified approach to the subject. First nine Units covering physical and inorganic chemistry portions are included in Part I while organic chemistry portion comprising of seven Units is included in Part II of the book. The approach of presentation of the subject matter discourages students from rote memorisation. The subject has in fact, been organised around the laws and principles of chemistry. As students master these laws and principles, they will soon get to the point where they can predict much of what will come.

Efforts have been directed towards making the subject stimulating and exciting by references to the historical developments and its usefulness to our lives, wherever appropriate. The text is well illustrated with examples from surrounding environment to facilitate grasping of the qualitative and quantitative aspects of the concept easily. Physical data are given in SI units throughout the book to make comparison of various properties easier. IUPAC system of nomenclature has been followed along with the common names. Structural formulae of chemical compounds showing functional/coordinating groups in different colours are drawn using electronic system. Each Unit has a good number of examples, as illustrations, with their solutions and some intext questions, the answers of some of which are given at the end of the Unit. The end of Unit exercises are designed to apply important principles and provoke thinking process to solve them. Answers of some of these exercises are given at the end of the book.

A variety of materials, e.g., biographical sketches of some scientists, additional information related to a particular topic, etc., is given in boxes with a deep yellow coloured bar. This boxed material with a 'deep yellow bar' is to bring additional life to the topic. However, it is non-evaluative. The structures of some of the more complex compounds incorporated in the book are for understanding their chemistry. As their reproduction would lead to memorisation, it is also a non-evaluative portion of the text.

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The information part has been significantly reduced and, wherever possible, it has been substantiated with facts. However, it is necessary for students to be aware of commercially important chemicals, their processes of manufacture and sources of raw materials. This leads to descriptive material in the book. Attempts have been made to make descriptions of such compounds interesting by considering their structures and reactivity. Thermodynamics, kinetics and electrochemical aspects have been applied to a few chemical reactions which should be beneficial to students for understanding why a particular reaction happened and why a particular property is exhibited by the product. There is currently great awareness of environmental and energy issues which are directly related to chemistry. Such issues have been highlighted and dealt with at appropriate places in the book.

A team of experts constituted by the NCERT has developed the manuscript of the book. It gives me great pleasure to acknowledge the valuable contribution of all the members of this team. I also acknowledge the valuable and relentless contribution of the editors in bringing the book to the present shape. I also acknowledge with thanks the dedicated efforts and valuable contribution of Professor Brahm Parkash, who not only coordinated the entire programme but also actively involved in writing and editing of this book. Thanks are also due to the participating teachers and subject experts of the review workshop for their contribution, which has helped us to make the book learner friendly. Also, I thank the technical and administrative staff of the NCERT for their support in the entire process.

The team of this textbook development programme hopes that the book stimulates its readers and makes them feel the excitement and fascination for this subject. Efforts have been made to bring out this book error-free. Nevertheless, it is recognised that in a book of this complexity, there could inevitably be occasional errors. It will always be a pleasure to hear about them from readers to take necessary steps to rectify them.

B.L. KHANDELWAL

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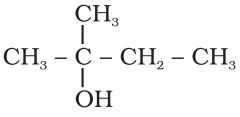
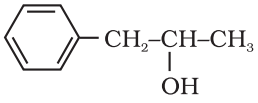
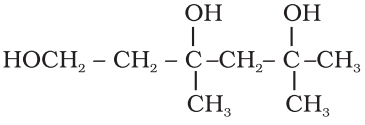
Answers to Some Questions in Exercises

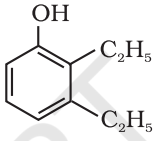
UNIT 7

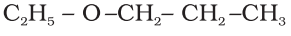
7.1 (i) 2,2,4-Trimethylpentan –3-ol
(ii) 5-Ethylheptane –2, 4-diol
(iii) Butane –2,3-diol
(iv) Propane –1,2,3,-triol
(v) 2- Methylphenol
(vi) 4-Methylphenol
(vii) 2,5 – Dimethylphenol
(viii) 2,6-Dimethylphenol
(ix) 1-Methoxy-2-methylpropane
(x) Ethoxybenzene
(xi) 1-phenoxyheptane
(xii) 2 –Ethoxybutane

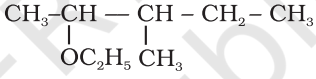
7.2 (i) 

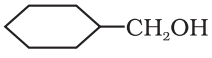
(ii) 

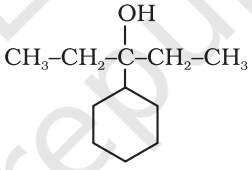
(iii) 

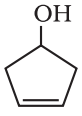
(iv) 

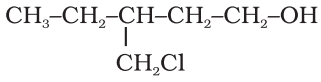
(v) 

(vi) 

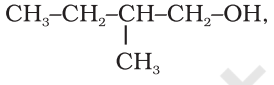
(vii) 

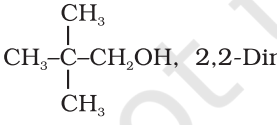
(viii) 

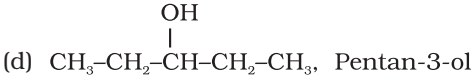
(ix) 

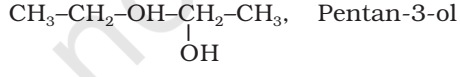
(x) 

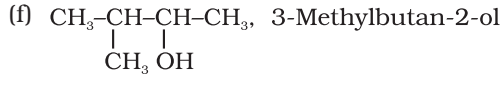
7.3 (i) (a) $CH_3CH_2CH_2CH_2CH_2OH$, Pentan-1-ol;

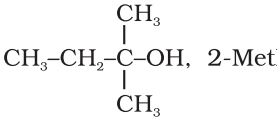
(b) 
2-Methylbutan-1-ol;

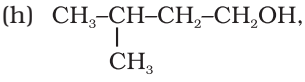
(c) 
2,2-Dimethylpropan-1-ol

(d) 
Pentan-3-ol

(e) 
Pentan-3-ol

(f) 
3-Methylbutan-2-ol

(g) 
2-Methylbutan-2-ol

(h) 
3-Methylbutan-1-ol

7.4 Hydrogen bonding in propanol.

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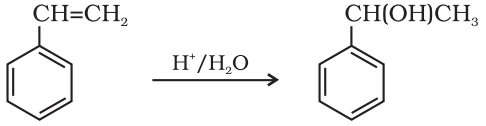
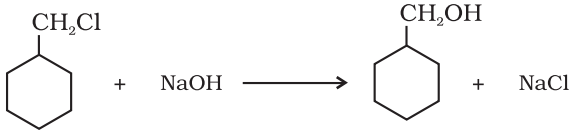
7.5 Hydrogen bonding between alcohol and water molecules.

7.8 o-Nitrophenol is steam volatile because of intramolecular hydrogen bonding.

7.12 **Hint:** Carryout sulphonation followed by nucleophilic substitution.

7.13 (i) 

(ii) 

(iii) $CH_3(CH_2)_4Cl + NaOH \longrightarrow CH_3(CH_2)_4OH + NaCl$

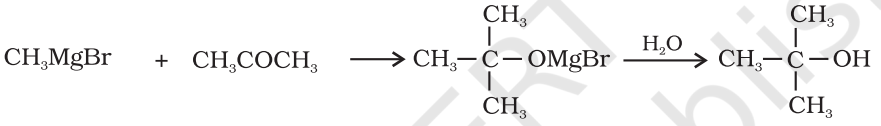
7.14 Reaction with (i) sodium and (ii) sodium hydroxide

7.15 Due to electron withdrawing effect of nitro group and electron releasing effect of methoxy group.

7.20 (i) Hydration of Propene.

(ii) By nucleophilic substitution of –Cl in benzyl chloride using dilute NaOH.

(iii) $C_2H_5MgBr + HCHO \rightarrow C_2H_5CH_2OMgBr \xrightarrow{H_2O} C_2H_5CH_2OH$

(iv) 

7.23 (i) 1-Ethoxy-2-methylpropane.

(ii) 2-Chloro-1-methoxyethane.

(iii) 4-Nitroanisole.

(iv) 1-Methoxypropane.

(v) 1-Ethoxy-4,4-dimethylcyclohexane.

(vi) Ethoxybenzene.

UNIT 8

8.2 (i) 4-Methylpentanal

(ii) 6-Chloro-4-ethylhexan-3-one

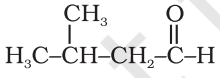
(iii) But-2-enal

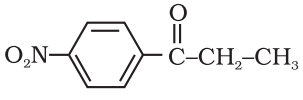
(iv) Pentane-2,4-dione

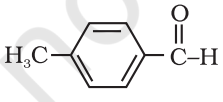
(v) 3,3,5-Trimethylhexan-2-one

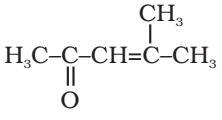
(vi) 3,3-Dimethylbutanoic acid

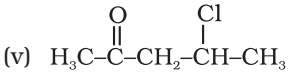
(vii) Benzene –1,4-dicarbaldehyde

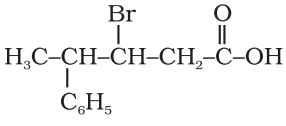
8.3 (i) 

(ii) 

(iii) 

(iv) 

(v) 

(vi) 

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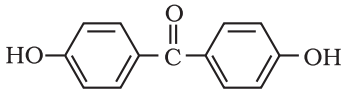
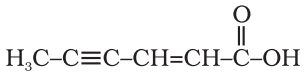
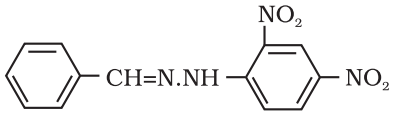
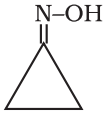
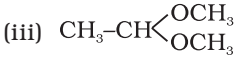
(vii) 

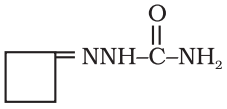
(viii) 

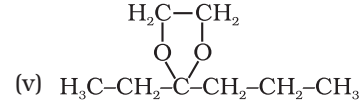
8.4 (i) Heptan-2-one (ii) 4-Bromo-2-methylhexanal (iii) Heptanal
(iv) 3-Phenylprop-2-enal (v) Cyclopentanecarbaldehyde (vi) Diphenylmethanone

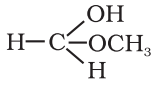
8.5 (i) 

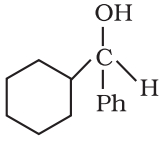
(ii) 

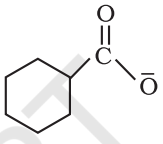
(iii) 

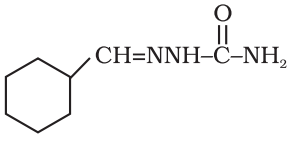
(iv) 

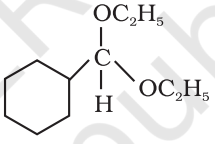
(v) 

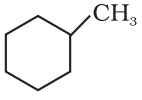
(vi) 

8.6 (i) 

(ii) 

(iii) 

(iv) 

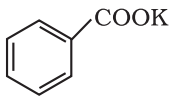
(v) 

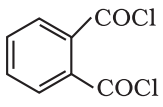
8.7 (ii), (v), (vi), (vii): Aldol condensation. (i), (iii), (ix) Cannizaro reaction. (iv), (viii) Neither.

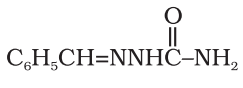
8.10 2-Ethylbenzaldehyde (draw the structure yourself).

8.11 (A) $CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3$, butyl butanoate.
(B) $CH_3CH_2CH_2$ COOH (C) $CH_3CH_2CH_2CH_2OH$. Write equation yourself.

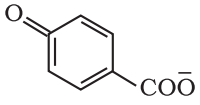
8.12 (i) Di-tert-butyl ketone < Methyl tert-butyl ketone < Acetone < Acetaldehyde
(ii) $(CH_3)_2CHCOOH$ < $CH_3CH_2CH_2COOH$ < $CH_3CH(Br)CH_2COOH$ < $CH_3CH_2CH(Br)COOH$
(iii) 4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid.

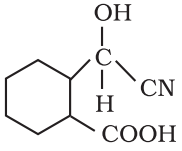
8.17 (i) 

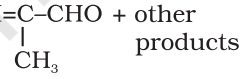
(ii) 

(iii) 

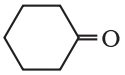
(iv) $C_6H_5COCl–AlCl_3$

(v) 

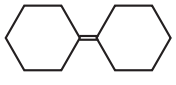
(vi) 

(vii) 

(viii) $CH_3CH(OH)CH_2COOC_2H_5$

(ix) 

(x) 1. BH_3; 2. $H_2O_2/\bar{O}H$; 3. PCC

(xi) 

8.19 The compound is methyl ketone and its structure would be: $CH_3COCH_2CH_2CH_3$

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UNIT 9

9.1 (i) 1-methylethylamine or propan-2-amine (ii) Propan-1-amine
(iii) N-methyl-2-methylethylamine or N-methylpropan-2-amine (iv) 2-methylpropan-2-amine
(v) N-methylbenzenamine or N-methylaniline (vi) N-Ethyl-N-methylethanamine
(vii) 3-Bromoaniline or 3-Bromobenzenamine

9.4 (i) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$
(ii) $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$
(iii) (a) p-nitroaniline < aniline < p-toluidine
(b) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$
(iv) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$ (v) $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$
(vi) $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

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Unit

6

Haloalkanes and Haloarenes

Objectives

After studying this Unit, you will be able to

- name haloalkanes and haloarenes according to the IUPAC system of nomenclature from their given structures;
- describe the reactions involved in the preparation of haloalkanes and haloarenes and understand various reactions that they undergo;
- correlate the structures of haloalkanes and haloarenes with various types of reactions;
- use stereochemistry as a tool for understanding the reaction mechanism;
- appreciate the applications of organo-metallic compounds;
- highlight the environmental effects of polyhalogen compounds.

Halogenated compounds persist in the environment due to their resistance to breakdown by soil bacteria.

The replacement of hydrogen atom(s) in an aliphatic or aromatic hydrocarbon by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively. Haloalkanes contain halogen atom(s) attached to the sp^3 hybridised carbon atom of an alkyl group whereas haloarenes contain halogen atom(s) attached to sp^2 hybridised carbon atom(s) of an aryl group. Many halogen containing organic compounds occur in nature and some of these are clinically useful. These classes of compounds find wide applications in industry as well as in day-to-day life. They are used as solvents for relatively non-polar compounds and as starting materials for the synthesis of wide range of organic compounds. Chlorine containing antibiotic, *chloramphenicol*, produced by microorganisms is very effective for the treatment of typhoid fever. Our body produces iodine containing hormone, *thyroxine*, the deficiency of which causes a disease called *goiter*. Synthetic halogen compounds, *viz.* chloroquine is used for the treatment of malaria; halothane is used as an anaesthetic during surgery. Certain fully fluorinated compounds are being considered as potential blood substitutes in surgery.

In this Unit, you will study the important methods of preparation, physical and chemical properties and uses of organohalogen compounds.

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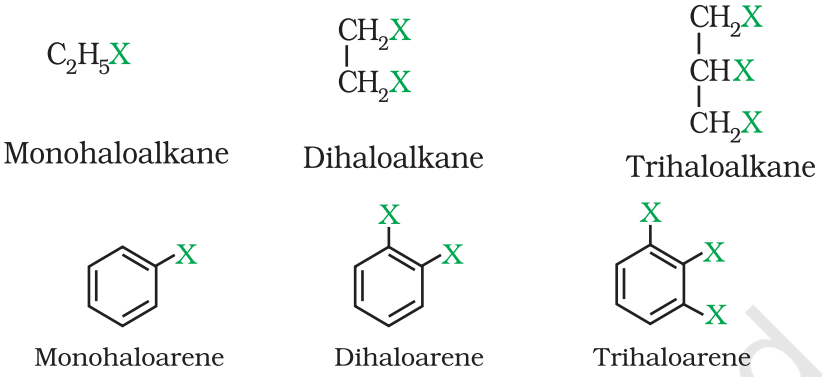
6.1 Classification

Haloalkanes and haloarenes may be classified as follows:

6.1.1 On the Basis of Number of Halogen Atoms

These may be classified as mono, di, or polyhalogen (tri-,tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures. For example,



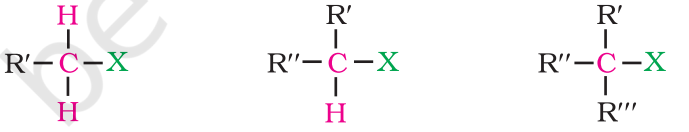
Monohalocompounds may further be classified according to the hybridisation of the carbon atom to which the halogen is bonded, as discussed below.

6.1.2 Compounds Containing sp^3 C—X Bond (X= F, Cl, Br, I)

This class includes

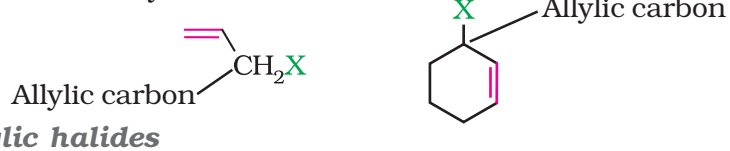
(a) Alkyl halides or haloalkanes (R—X)

In alkyl halides, the halogen atom is bonded to an alkyl group (R). They form a homologous series represented by $C_nH_{2n+1}X$. They are further classified as primary, secondary or tertiary according to the nature of carbon to which halogen is attached. If halogen is attached to a primary carbon atom in an alkyl halide, the alkyl halide is called primary alkyl halide or 1° alkyl halide. Similarly, if halogen is attached to secondary or tertiary carbon atom, the alkyl halide is called secondary alkyl halide (2°) and tertiary (3°) alkyl halide, respectively.



(b) Allylic halides

These are the compounds in which the halogen atom is bonded to an sp^3-hybridised carbon atom adjacent to carbon-carbon double bond (C=C) *i.e.* to an allylic carbon.



(c) Benzylic halides

These are the compounds in which the halogen atom is bonded to an sp^3-hybridised carbon atom attached to an aromatic ring.

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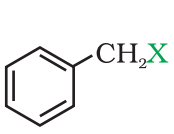
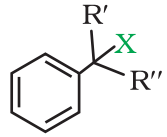


(1°)



R′ = CH_3, R″ = H (2°)

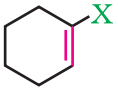
R′ = R″ = CH_3 (3°)

6.1.3 Compounds Containing sp^2 C—X Bond

This class includes:

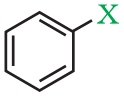
(a) Vinylic halides

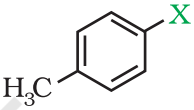
These are the compounds in which the halogen atom is bonded to a sp^2-hybridised carbon atom of a carbon-carbon double bond (C = C).



(b) Aryl halides

These are the compounds in which the halogen atom is directly bonded to the sp^2-hybridised carbon atom of an aromatic ring.

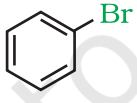
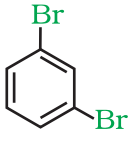
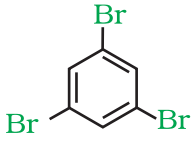


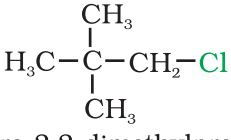
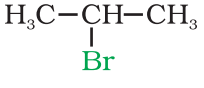


6.2 Nomenclature

Having learnt the classification of halogenated compounds, let us now learn how these are named. The common names of alkyl halides are derived by naming the alkyl group followed by the name of halide. In the IUPAC system of nomenclature, alkyl halides are named as halosubstituted hydrocarbons. For mono halogen substituted derivatives of benzene, common and IUPAC names are the same. For dihalogen derivatives, the prefixes *o*-, *m*-, *p*- are used in common system but in IUPAC system, as you have learnt in Class XI, the numerals 1,2; 1,3 and 1,4 are used.

	$CH_3CH_2CH_2Br$	$H_3C–\underset{\displaystyle Cl}{\underset{\vert}{CH}}–CH_3$	$H_3C–\underset{\displaystyle H_3C–CH_2Cl}{\underset{\vert}{CH}}$
Common name:	n-Propyl bromide	Isopropyl chloride	Isobutyl chloride
IUPAC name:	1-Bromopropane	2-Chloropropane	1-Chloro-2-methylpropane

			
Common name:	Bromobenzene	*m*-Dibromobenzene	*sym*-Tribromobenzene
IUPAC name:	Bromobenzene	1,3-Dibromobenzene	1,3,5-Tribromobenzene

		
IUPAC name:	1-Chloro-2,2-dimethylpropane	2-Bromopropane

The dihaloalkanes having the same type of halogen atoms are named as alkylidene or alkylene dihalides. The dihalo-compounds having both the halogen atoms are further classified as geminal halides or gem-dihalides when both the halogen atoms are present on the same carbon atom of the

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chain and vicinal halides or vic-dihalides when halogen atoms are present on adjacent carbon atoms. In common name system, gem-dihalides are named as alkylidene halides and vic-dihalides are named as alkylene dihalides. In IUPAC system, they are named as dihaloalkanes.

	$H_3C-CHCl_2$	$H_2C(Cl)-CH_2(Cl)$
Common name:	Ethylidene chloride (gem-dihalide)	Ethylene dichloride (vic-dihalide)
IUPAC name:	1, 1-Dichloroethane	1, 2-Dichloroethane

Some common examples of halocompounds are mentioned in Table 6.1.

Table 6.1: Common and IUPAC Names of some Halides

Structure	Common name	IUPAC name
$CH_3CH_2CH(Cl)CH_3$	sec-Butyl chloride	2-Chlorobutane
$(CH_3)_3CCH_2Br$	neo-Pentyl bromide	1-Bromo-2,2-dimethylpropane
$(CH_3)_3CBr$	tert-Butyl bromide	2-Bromo-2-methylpropane
$CH_2 = CHCl$	Vinyl chloride	Chloroethene
$CH_2 = CHCH_2Br$	Allyl bromide	3-Bromopropene
	o-Chlorotoluene	1-Chloro-2-methylbenzene or 2-Chlorotoluene
	Benzyl chloride	Chlorophenylmethane
CH_2Cl_2	Methylene chloride	Dichloromethane
$CHCl_3$	Chloroform	Trichloromethane
$CHBr_3$	Bromoform	Tribromomethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
$CH_3CH_2CH_2F$	n-Propyl fluoride	1-Fluoropropane

Example 6.1 Draw the structures of all the eight structural isomers that have the molecular formula $C_5H_{11}Br$. Name each isomer according to IUPAC system and classify them as primary, secondary or tertiary bromide.

Solution

$CH_3CH_2CH_2CH_2CH_2Br$	1-Bromopentane (1^o)
$CH_3CH_2CH_2CH(Br)CH_3$	2-Bromopentane(2^o)
$CH_3CH_2CH(Br)CH_2CH_3$	3-Bromopentane (2^o)
$(CH_3)_2CHCH_2CH_2Br$	1-Bromo-3-methylbutane (1^o)

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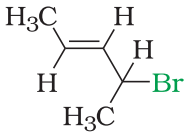
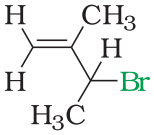
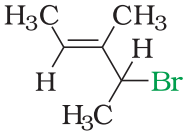
$(CH_3)_2CHCHBrCH_3$	2-Bromo-3-methylbutane(2°)
$(CH_3)_2CBrCH_2CH_3$	2-Bromo-2-methylbutane (3°)
$CH_3CH_2CH(CH_3)CH_2Br$	1-Bromo-2-methylbutane(1°)
$(CH_3)_3CCH_2Br$	1-Bromo-2,2-dimethylpropane (1°)

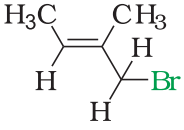
Example 6.2

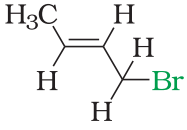
Write IUPAC names of the following:

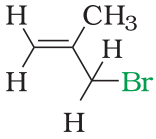
(i) 

(ii) 

(iii) 

(iv) 

(v) 

(vi) 

Solution

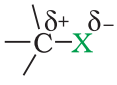
(i) 4-Bromopent-2-ene
(ii) 3-Bromo-2-methylbut-1-ene
(iii) 4-Bromo-3-methylpent-2-ene
(iv) 1-Bromo-2-methylbut-2-ene
(v) 1-Bromobut-2-ene
(vi) 3-Bromo-2-methylpropene

Intext Question

6.1 Write structures of the following compounds:
(i) 2-Chloro-3-methylpentane
(ii) 1-Chloro-4-ethylcyclohexane
(iii) 4-tert. Butyl-3-iodoheptane
(iv) 1,4-Dibromobut-2-ene
(v) 1-Bromo-4-sec. butyl-2-methylbenzene.

6.3 Nature of C-X Bond

Halogen atoms are more electronegative than carbon, therefore, carbon-halogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.



As we go down the group in the periodic table, the size of halogen atom increases. Fluorine atom is the smallest and iodine atom is the largest. Consequently the carbon-halogen bond length also increases from C—F to C—I. Some typical bond lengths, bond enthalpies and dipole moments are given in Table 6.2.
Alkyl halides are best prepared from alcohols, which are easily accessible.

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Table 6.2: Carbon-Halogen (C—X) Bond Lengths, Bond Enthalpies and Dipole Moments

Bond	Bond length/pm	C-X Bond enthalpies/ kJmol^{-1}	Dipole moment/Debye
CH_3–F	139	452	1.847
CH_3– Cl	178	351	1.860
CH_3–Br	193	293	1.830
CH_3–I	214	234	1.636

6.4 Methods of Preparation of Haloalkanes

6.4.1 From Alcohols

The hydroxyl group of an alcohol is replaced by halogen on reaction with concentrated halogen acids, phosphorus halides or thionyl chloride. Thionyl chloride is preferred because in this reaction alkyl halide is formed along with gases SO_2 and HCl. The two gaseous products are escapable, hence, the reaction gives pure alkyl halides. The reactions of primary and secondary alcohols with HCl require the presence of a catalyst, $ZnCl_2$. With tertiary alcohols, the reaction is conducted by simply shaking the alcohol with concentrated HCl at room temperature. Constant boiling with HBr (48%) is used for preparing alkyl bromide. Good yields of R—I may be obtained by heating alcohols with sodium or potassium iodide in 95% orthophosphoric acid. The order of reactivity of alcohols with a given haloacid is 3°>2°>1°. Phosphorus tribromide and triiodide are usually generated *in situ* (produced in the reaction mixture) by the reaction of red phosphorus with bromine and iodine respectively.

$$R\text{–}OH + HCl \xrightarrow{ZnCl_2} R\text{–}Cl + H_2O$$

$$R\text{–}OH + NaBr + H_2SO_4 \longrightarrow R\text{–}Br + NaHSO_4 + H_2O$$

$$3R\text{–}OH + PX_3 \longrightarrow 3R\text{–}X + H_3PO_3 \quad (X = Cl, Br)$$

$$R\text{–}OH + PCl_5 \longrightarrow R\text{–}Cl + POCl_3 + HCl$$

$$R\text{–}OH \xrightarrow[X_2=Br_2,I_2]{\text{red } P/X_2} R\text{–}X$$

$$R\text{–}OH + SOCl_2 \longrightarrow R\text{–}Cl + SO_2 + HCl$$

The preparation of alkyl chloride is carried out either by passing dry hydrogen chloride gas through a solution of alcohol or by heating a mixture of alcohol and concentrated aqueous halogen acid.

The above methods are not applicable for the preparation of aryl halides because the carbon-oxygen bond in phenols has a partial double bond character and is difficult to break being stronger than a single bond.

6.4.2 From Hydrocarbons

(I) From alkanes by free radical halogenation

Free radical chlorination or bromination of alkanes gives a complex mixture of isomeric mono- and polyhaloalkanes, which is difficult to

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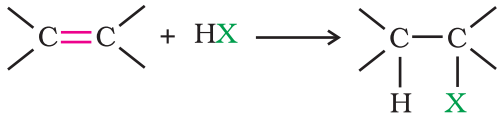
separate as pure compounds. Consequently, the yield of any single compound is low.

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

(II) From alkenes

(i) *Addition of hydrogen halides*: An alkene is converted to corresponding alkyl halide by reaction with hydrogen chloride, hydrogen bromide or hydrogen iodide.



Propene yields two products, however only one predominates as per Markovnikov's rule. (Unit 13, Class XI)

$$CH_3CH=CH_2 + H{-}I \longrightarrow \underset{\text{minor}}{CH_3CH_2CH_2I} + \underset{\text{major}}{CH_3CHICH_3}$$

(ii) *Addition of halogens:* In the laboratory, addition of bromine in CCl_4 to an alkene resulting in discharge of reddish brown colour of bromine constitutes an important method for the detection of double bond in a molecule. The addition results in the synthesis of *vic*-dibromides, which are colourless (Unit 9, Class XI).

Example 6.3

Identify all the possible monochloro structural isomers expected to be formed on free radical monochlorination of $(CH_3)_2CHCH_2CH_3$.

Solution

In the given molecule, there are four different types of hydrogen atoms. Replacement of these hydrogen atoms will give the following

$(CH_3)_2CHCH_2CH_2Cl$ $(CH_3)_2CHCH(Cl)CH_3$

$(CH_3)_2C(Cl)CH_2CH_3$ $CH_3CH(CH_2Cl)CH_2CH_3$

6.4.3 Halogen Exchange

Alkyl iodides are often prepared by the reaction of alkyl chlorides/ bromides with NaI in dry acetone. This reaction is known as **Finkelstein** reaction.

$$R{-}X + NaI \longrightarrow R{-}I + NaX$$

X=Cl, Br

NaCl or NaBr thus formed is precipitated in dry acetone. It facilitates the forward reaction according to Le Chatelier's Principle.

The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as

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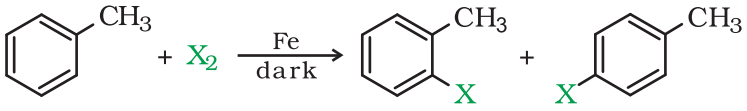
AgF, Hg_2F_2, CoF_2 or SbF_3. The reaction is termed as **Swarts** reaction.

$$H_3C{-}Br + AgF \longrightarrow H_3C{-}F + AgBr$$

6.5 Preparation of Haloarenes

(i) From hydrocarbons by electrophilic substitution

Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts like iron or iron(III) chloride.

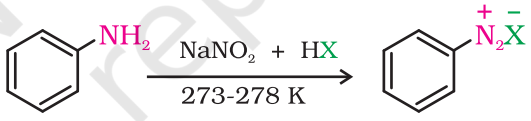


o-Halotoluene *p*-Halotoluene

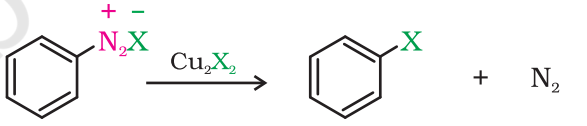
The *ortho* and *para* isomers can be easily separated due to large difference in their melting points. Reactions with iodine are reversible in nature and require the presence of an oxidising agent (HNO_3, HIO_4) to oxidise the HI formed during iodination. Fluoro compounds are not prepared by this method due to high reactivity of fluorine.

(ii) From amines by Sandmeyer's reaction

When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed. Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by –Cl or –Br.

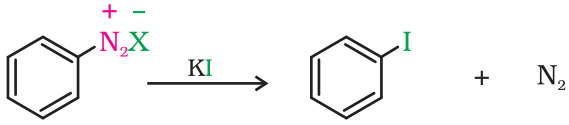


Benzene diazonium halide



Aryl halide X = Cl, Br

Replacement of the diazonium group by iodine does not require the presence of cuprous halide and is done simply by shaking the diazonium salt with potassium iodide.



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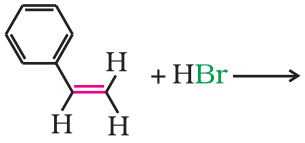
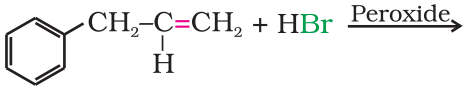
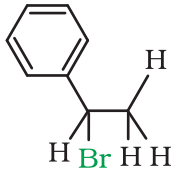
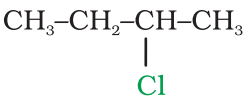
Example 6.4 Write the products of the following reactions:

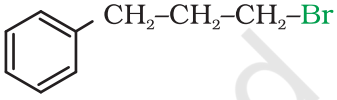
(i)  (ii) $CH_3–CH_2–CH=CH_2 + HCl \longrightarrow$

(iii) 

Solution

(i) 

(ii) 

(iii) 

Intext Questions

6.2 Why is sulphuric acid not used during the reaction of alcohols with KI?

6.3 Write structures of different dihalogen derivatives of propane.

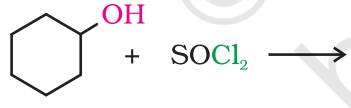
6.4 Among the isomeric alkanes of molecular formula C_5H_{12}, identify the one that on photochemical chlorination yields

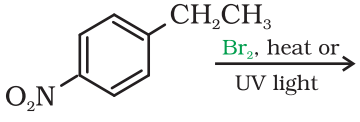
(i) A single monochloride.

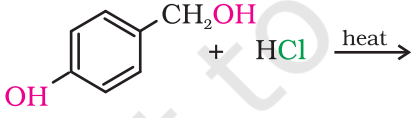
(ii) Three isomeric monochlorides.

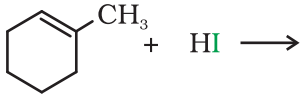
(iii) Four isomeric monochlorides.

6.5 Draw the structures of major monohalo products in each of the following reactions:

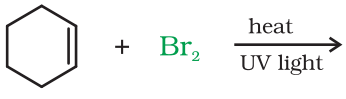
(i) 

(ii) 

(iii) 

(iv) 

(v) $CH_3CH_2Br + NaI \longrightarrow$

(vi) 

6.6 Physical Properties

Alkyl halides are colourless when pure. However, bromides and iodides develop colour when exposed to light. Many volatile halogen compounds have sweet smell.

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Melting and boiling points

Methyl chloride, methyl bromide, ethyl chloride and some chlorofluoromethanes are gases at room temperature. Higher members are liquids or solids. As we have already learnt, molecules of organic halogen compounds are generally polar. Due to greater polarity as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole-dipole and van der Waals) are stronger in the halogen derivatives. That is why the boiling points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass.

The attractions get stronger as the molecules get bigger in size and have more electrons. The pattern of variation of boiling points of different halides is depicted in Fig. 6.1. For the same alkyl group, the boiling points of alkyl halides decrease in the order: RI> RBr> RCl> RF. This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.

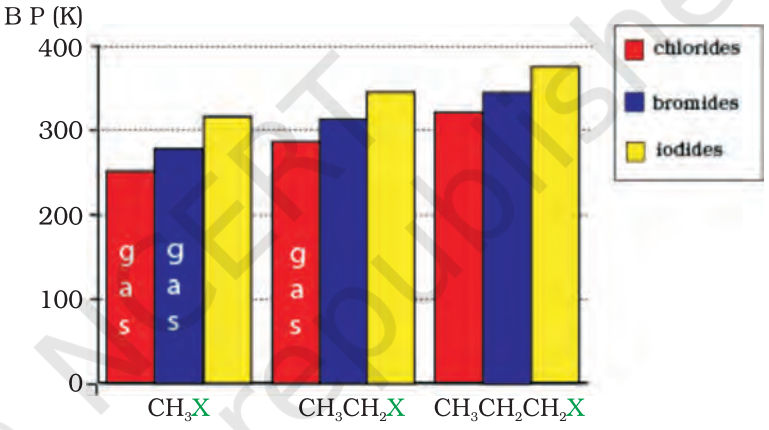

Fig. 6.1: *Comparison of boiling points of some alkyl halides*

The boiling points of isomeric haloalkanes decrease with increase in branching. For example, 2-bromo-2-methylpropane has the lowest boiling point among the three isomers.

	$CH_3CH_2CH_2CH_2Br$	$CH_3CH_2\underset{\displaystyle Br}{\underset{\vert}{C}}HCH_3$	$H_3C-\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\vert}{C}}}-CH_3$ (Br)
b.p./K	375	364	346

Boiling points of isomeric dihalobenzenes are very nearly the same. However, the *para*-isomers are high melting as compared to their *ortho*- and *meta*-isomers. It is due to symmetry of *para*-isomers that fits in crystal lattice better as compared to *ortho*- and *meta*-isomers.

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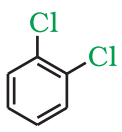
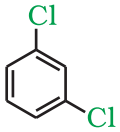

b.p /K	453	446	448
m.p/K	256	249	323

Density

Bromo, iodo and polychloro derivatives of hydrocarbons are heavier than water. The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms (Table 6.3).

Table 6.3: Density of Some Haloalkanes

Compound	Density (g/mL)	Compound	Density (g/mL)
n–C_3H_7Cl	0.89	CH_2Cl_2	1.336
n–C_3H_7Br	1.335	$CHCl_3$	1.489
n-C_3H_7I	1.747	CCl_4	1.595

Solubility

The haloalkanes are very slightly soluble in water. In order to dissolve haloalkane in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. Less energy is released when new attractions are set up between the haloalkane and the water molecules as these are not as strong as the original hydrogen bonds in water. As a result, the solubility of haloalkanes in water is low. However, haloalkanes tend to dissolve in organic solvents because the new intermolecular attractions between haloalkanes and solvent molecules have much the same strength as the ones being broken in the separate haloalkane and solvent molecules.

Intext Question

6.6 Arrange each set of compounds in order of increasing boiling points.

(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

(ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

6.7 Chemical Reactions

The reactions of haloalkanes may be divided into the following categories:

1. Nucleophilic substitution
2. Elimination reactions
3. Reaction with metals.

6.7.1 Reactions of Haloalkanes

(1) Nucleophilic substitution reactions

You have learnt in Class XI that nucleophiles are electron rich species. Therefore, they attack at that part of the substrate molecule which is electron deficient. The reaction in which a nucleophile replaces

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already existing nucleophile in a molecule is called nucleophilic substitution reaction. Haloalkanes are substrate in these reactions. In this type of reaction, a nucleophile reacts with haloalkane (the substrate) having a partial positive charge on the carbon atom bonded to halogen. A substitution reaction takes place and halogen atom, called leaving group departs as halide ion. Since the substitution reaction is initiated by a nucleophile, it is called nucleophilic substitution reaction.

It is one of the most useful classes of organic reactions of alkyl halides in which halogen is bonded to sp^3 hybridised carbon. The products formed by the reaction of haloalkanes with some common nucleophiles are given in Table 6.4.

Table 6.4: Nucleophilic Substitution of Alkyl Halides (R–X)

$$R - X + Nu^- \rightarrow R - Nu + X^-$$

Reagent	Nucleophile (Nu^-)	Substitution product R–Nu	Class of main product
NaOH (KOH)	HO^-	ROH	Alcohol
H_2O	H_2O	ROH	Alcohol
NaOR′	$R'O^-$	ROR′	Ether
NaI	I^-	R—I	Alkyl iodide
NH_3	NH_3	RNH_2	Primary amine
$R'NH_2$	$R'NH_2$	RNHR′	Sec. amine
R′R″NH	R′R″NH	RNR′R″	Tert. amine
KCN	$\bar{C}\equiv N$:	RCN	Nitrile (cyanide)
AgCN	Ag-CN:	RNC (isocyanide)	Isonitrile
KNO_2	O=N—O	R—O—N=O	Alkyl nitrite
$AgNO_2$	Ag—Ö—N=O	$R—NO_2$	Nitroalkane
R′COOAg	$R'COO^-$	R′COOR	Ester
$LiAlH_4$	H	RH	Hydrocarbon
R'^-M^+	R'^-	RR′	Alkane

Groups like cyanides and nitrites possess two nucleophilic centres and are called ***ambident nucleophiles.*** Actually cyanide group is a hybrid of two contributing structures and therefore can act as a nucleophile in two different ways [$^{\ominus}C\equiv N \leftrightarrow :C=N^{\ominus}$], *i.e.,* linking through

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Example 6.5

Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.

Solution

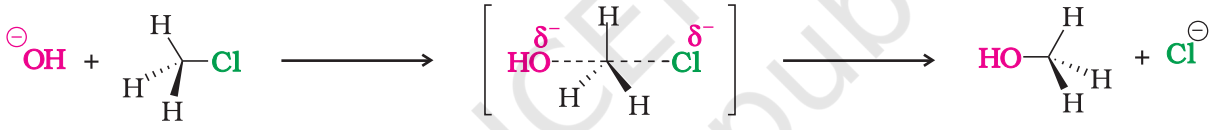
KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C—C bond is more stable than C—N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.

carbon atom resulting in alkyl cyanides and through nitrogen atom leading to isocyanides. Similarly nitrite ion also represents an ambident nucleophile with two different points of linkage [$^{-}O—\ddot{N}=O$]. The linkage through oxygen results in alkyl nitrites while through nitrogen atom, it leads to nitroalkanes.

Mechanism: This reaction has been found to proceed by two different mechanims which are described below:

(a) Substitution nucleophilic bimolecular (S_N2)

The reaction between CH_3Cl and hydroxide ion to yield methanol and chloride ion follows a second order kinetics, i.e., the rate depends upon the concentration of both the reactants.



The solid wedge represents the bond coming out of the paper, dashed line going down the paper and a straight line representing bond in the plane of the paper.

The above reaction can be represented diagrammatically as shown in Fig. 6.2.

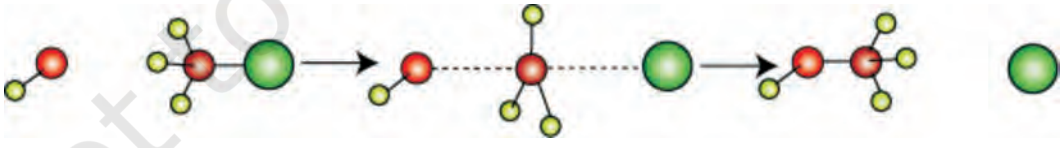


Fig. 6.2: *Red ball represents the incoming hydroxide ion and green ball represents the outgoing halide ion*

In the year 1937, Edward Davies Hughes and Sir Christopher Ingold proposed a mechanism for an S_N2 reaction.

It depicts a bimolecular nucleophilic substitution (S_N2) reaction; the incoming nucleophile interacts with alkyl halide causing the carbon-halide bond to break and a new bond is formed between carbon and attacking nucleophile. Here it is C-O bond formed between C and -OH. These two processes take place simultaneously in a

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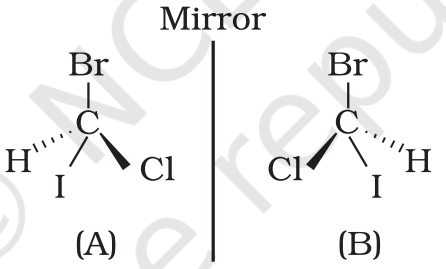
single step and no intermediate is formed. As the reaction progresses and the bond between the incoming nucleophile and the carbon atom starts forming, the bond between carbon atom and leaving group weakens. As this happens, the three carbon-hydrogen bonds of the substrate start moving away from the attacking nucleophile. In transition state all the three C-H bonds are in the same plane and the attacking and leaving nucleophiles are partially attached to the carbon. As the attacking nucleophile approaches closer to the carbon, C-H bonds still keep on moving in the same direction till the attacking nucleophile attaches to carbon and leaving group leaves the carbon. As a result configuration is inverted, the configuration (See box) of carbon atom under attack inverts in much the same way as an umbrella is turned inside out when caught in a strong wind. This process is called as **inversion of configuration**. In the transition state, the carbon atom is simultaneously bonded to incoming nucleophile and the outgoing leaving group. Such structures are unstable and cannot be isolated. Thus, in the transition state, carbon is simultaneously bonded to five atoms.

Configuration

Spacial arrangement of functional groups around carbon is called its configuration. See the structures (A) and (B) given below carefully.



These are the two structures of the same compound. They differ in spacial arrangement of functional groups attached to carbon. Structure (A) is mirror image of Structure (B). We say configuration of carbon in structure (A) is mirror image of the configuration of carbon in structure (B).

Hughes worked under Ingold and earned a D.Sc. degree from the University of London.

Since this reaction requires the approach of the nucleophile to the carbon bearing the leaving group, the presence of bulky substituents on or near the carbon atom have a dramatic inhibiting effect. Of the simple alkyl halides, methyl halides react most rapidly in S_N2 reactions because there are only three small hydrogen atoms. Tertiary halides are the least reactive because bulky groups hinder the approaching

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nucleophiles. Thus the order of reactivity followed is:
Primary halide > Secondary halide > Tertiary halide.

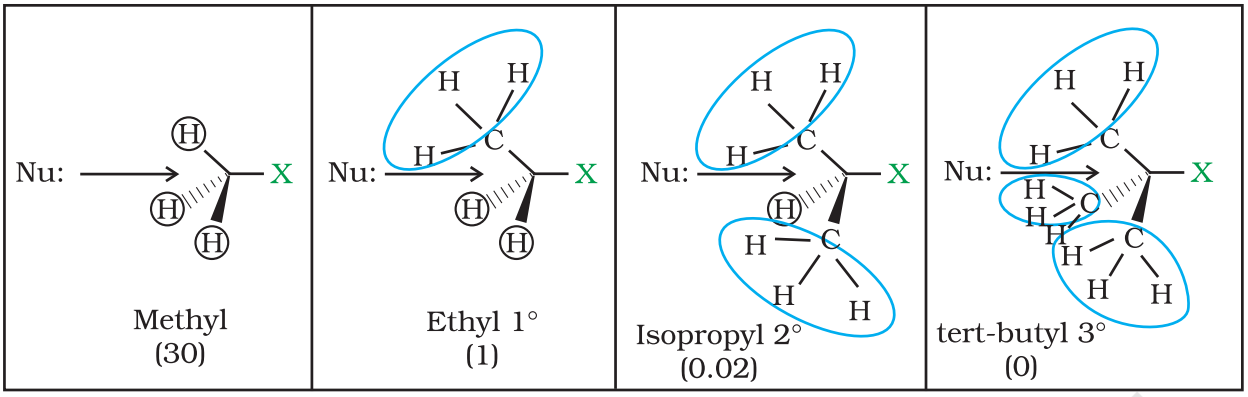


Fig.6.3: *Steric effects in S_N2 reaction. The relative rate of S_N2 reaction is given in parenthesis*

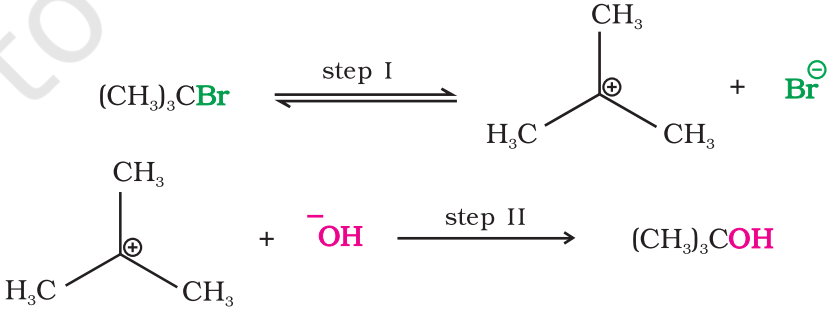
(b) Substitution nucleophilic unimolecular (S_N1)

S_N1 reactions are generally carried out in polar protic solvents (like water, alcohol, acetic acid, etc.). The reaction between *tert*-butyl bromide and hydroxide ion yields *tert*-butyl alcohol and follows the first order kinetics, *i.e.*, the rate of reaction depends upon the concentration of only one reactant, which is *tert*- butyl bromide.

$$(CH_3)_3CBr + {}^{-}OH \longrightarrow (CH_3)_3COH + Br^{-}$$

2-Bromo-2-methylpropane — 2-Methylpropan-2-ol

It occurs in two steps. In step I, the polarised C—Br bond undergoes slow cleavage to produce a carbocation and a bromide ion. The carbocation thus formed is then attacked by nucleophile in step II to complete the substitution reaction.



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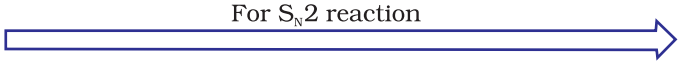
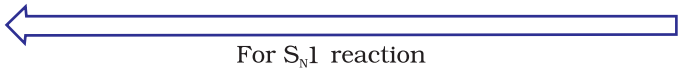
Step I is the slowest and reversible. It involves the C–Br bond breaking for which the energy is obtained through solvation of halide ion with the proton of protic solvent. Since the rate of reaction depends upon the slowest step, the rate of reaction depends only on the concentration of alkyl halide and not on the concentration of hydroxide ion. Further, greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction. In case of alkyl halides, 3^0 alkyl halides undergo S_N1 reaction very fast because of the high stability of 3^0 carbocations. We can sum up the order of reactivity of alkyl halides towards S_N1 and S_N2 reactions as follows:

For S_N2 reaction

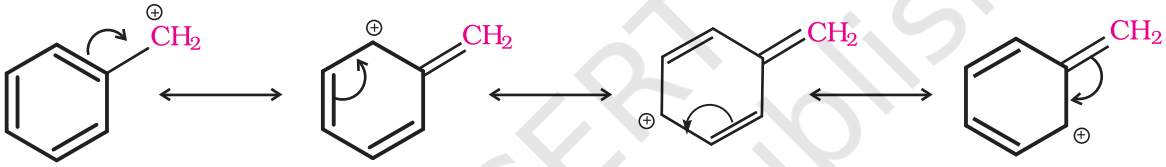


Tertiary halide; Secondary halide; Primary halide; CH_3X



For S_N1 reaction

For the same reasons, allylic and benzylic halides show high reactivity towards the S_N1 reaction. The carbocation thus formed gets stabilised through resonance (Unit 8, Class XI) as shown below:

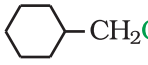


For a given alkyl group, the reactivity of the halide, R-X, follows the same order in both the mechanisms R–I> R–Br>R–Cl>>R–F.

Example 6.6

In the following pairs of halogen compounds, which would undergo S_N2 reaction faster?

Solution



It is primary halide and therefore undergoes S_N2 reaction faster.

As iodine is a better leaving group because of its large size, it will be released at a faster rate in the presence of incoming nucleophile.

Example 6.7

Predict the order of reactivity of the following compounds in S_N1 and S_N2 reactions:

(i) The four isomeric bromobutanes

(ii) $C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$

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Solution (i) $CH_3CH_2CH_2CH_2Br < (CH_3)_2CHCH_2Br < CH_3CH_2CH(Br)CH_3 < (CH_3)_3CBr$ (S_N1)

$CH_3CH_2CH_2CH_2Br > (CH_3)_2CHCH_2Br > CH_3CH_2CH(Br)CH_3 > (CH_3)_3CBr$ (S_N2)

Of the two primary bromides, the carbocation intermediate derived from $(CH_3)_2CHCH_2Br$ is more stable than derived from $CH_3CH_2CH_2CH_2Br$ because of greater electron donating inductive effect of $(CH_3)_2CH$- group. Therefore, $(CH_3)_2CHCH_2Br$ is more reactive than $CH_3CH_2CH_2CH_2Br$ in S_N1 reactions. $CH_3CH_2CH(Br)CH_3$ is a secondary bromide and $(CH_3)_3CBr$ is a tertiary bromide. Hence the above order is followed in S_N1. The reactivity in S_N2 reactions follows the reverse order as the steric hinderance around the electrophilic carbon increases in that order.

(ii) $C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$ (S_N1)

$C_6H_5C(CH_3)(C_6H_5)Br < C_6H_5CH(C_6H_5)Br < C_6H_5CH(CH_3)Br < C_6H_5CH_2Br$ (S_N2)

Of the two secondary bromides, the carbocation intermediate obtained from $C_6H_5CH(C_6H_5)Br$ is more stable than obtained from $C_6H_5CH(CH_3)Br$ because it is stabilised by two phenyl groups due to resonance. Therefore, the former bromide is more reactive than the latter in S_N1 reactions. A phenyl group is bulkier than a methyl group. Therefore, $C_6H_5CH(C_6H_5)Br$ is less reactive than $C_6H_5CH(CH_3)Br$ in S_N2 reactions.

(c) *Stereochemical aspects of nucleophilic substitution reactions*

In order to understand the stereochemical aspects of substitution reactions, we need to learn some basic stereochemical principles and notations (**optical activity, chirality, retention, inversion, racemisation,** etc.).

William Nicol (1768-1851) developed the first prism that produced plane polarised light.

(i) *Optical activity*: Plane of plane polarised light produced by passing ordinary light through Nicol prism is rotated when it is passed through the solutions of certain compounds. Such compounds are called **optically active** compounds. The angle by which the plane polarised light is rotated is measured by an instrument called polarimeter. If the compound rotates the plane of plane polarised light to the right, i.e., clockwise direction, it is called *dextrorotatory* (Greek for right rotating) or the *d*-form and is indicated by placing a positive (+) sign before the degree of rotation. If the light is rotated towards left (anticlockwise direction), the compound is said to be laevo-rotatory or the *l*-form and a negative (–) sign is placed before the degree of rotation. Such (+) and (–) isomers of a compound are called **optical isomers** and the phenomenon is termed as **optical isomerism**.

(ii) *Molecular asymmetry, chirality and enantiomers*: The observation of Louis Pasteur (1848) that crystals of certain compounds exist in the form of mirror images laid the foundation of modern stereochemistry. He demonstrated that aqueous solutions of both types of crystals showed optical rotation, equal in magnitude (for solution of equal concentration) but opposite in direction. He believed that this difference in optical activity was associated with the three dimensional arrangements of atoms in the molecules (**configurations**) of

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Jacobus Hendricus Van't Hoff (1852-1911) received the first Nobel Prize in Chemistry in 1901 for his work on solutions.

two types of crystals. Dutch scientist, *J. Van't Hoff* and French scientist, *C. Le Bel* in the same year (1874), independently argued that the spatial arrangement of four groups (valencies) around a central carbon is tetrahedral and if all the substituents attached to that carbon are different, the mirror image of the molecule is not superimposed (overlapped) on the molecule; such a carbon is called **asymmetric carbon** or **stereocentre**. The resulting molecule would lack symmetry and is referred to as asymmetric molecule. The asymmetry of the molecule along with non superimposability of mirror images is responsible for the optical activity in such organic compounds.

The symmetry and asymmetry are also observed in many day to day objects: a sphere, a cube, a cone, are all identical to their mirror images and can be superimposed. However, many objects are non superimposable on their mirror images. For example, your left and right hand look similar but if you put your left hand on your right hand by moving them in the same plane, they do not coincide. The objects which are non-superimposable on their mirror image (like a pair of hands) are said to be **chiral** and this property is known as **chirality**. Chiral molecules are optically active, while the objects, which are, superimposable on their mirror images are called **achiral.** These molecules are optically inactive.

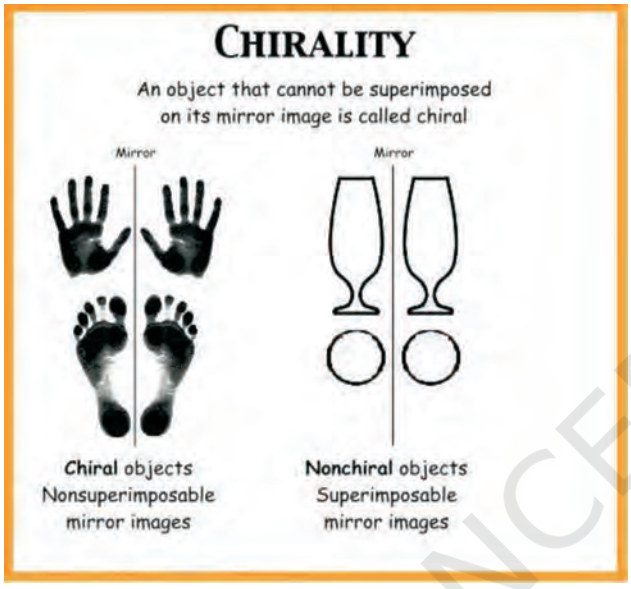

Fig 6.4: *Some common examples of chiral and achiral objects*

The above test of molecular chirality can be applied to organic molecules by constructing models and its mirror images or by drawing three dimensional structures and attempting to superimpose them in our minds. There are other aids, however, that can assist us in recognising chiral molecules. One such aid is the presence of a single asymmetric carbon atom. Let us consider two simple molecules propan-2-ol (Fig.6.5) and butan-2-ol (Fig.6.6) and their mirror images.

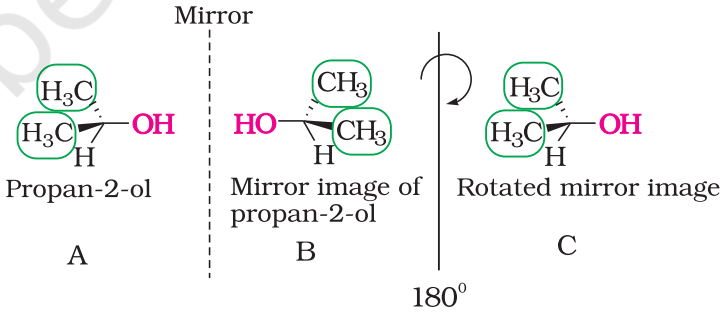

Fig 6.5: *B is mirror image of A; B is rotated by 180° and C is obtained; C is superimposable on A.*

As you can see very clearly, propan-2-ol (A) does not contain an asymmetric carbon, as all the four groups attached to the tetrahedral carbon are not different. We rotate the mirror image (B) of the molecule by 180° (structure C) and try to overlap the structure (C) with the structure (A), these structures completely overlap. Thus propan-2-ol is an **achiral** molecule.

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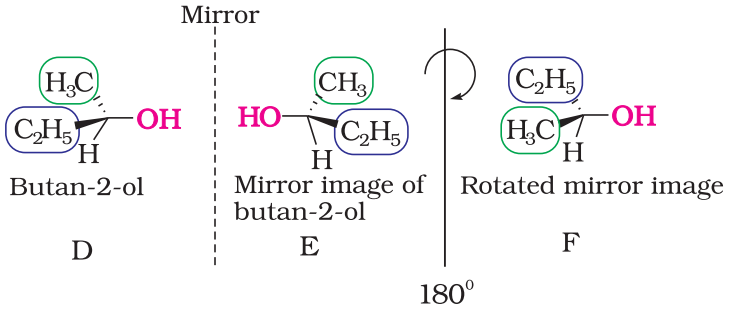


Fig 6.6: *E is mirror image of D; E is rotated by 180° to get F and F is non superimposable on its mirror image D.*

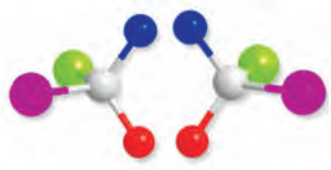


Fig. 6.7: *A chiral molecule and its mirror image*

Butan-2-ol has four different groups attached to the tetrahedral carbon and as expected is **chiral**. Some common examples of chiral molecules such as 2-chlorobutane, 2, 3-dihyroxypropanal, (OHC–CHOH–CH_2OH), bromochloro-iodomethane (BrClCHI), 2-bromopropanoic acid (H_3C–CHBr–COOH), etc.

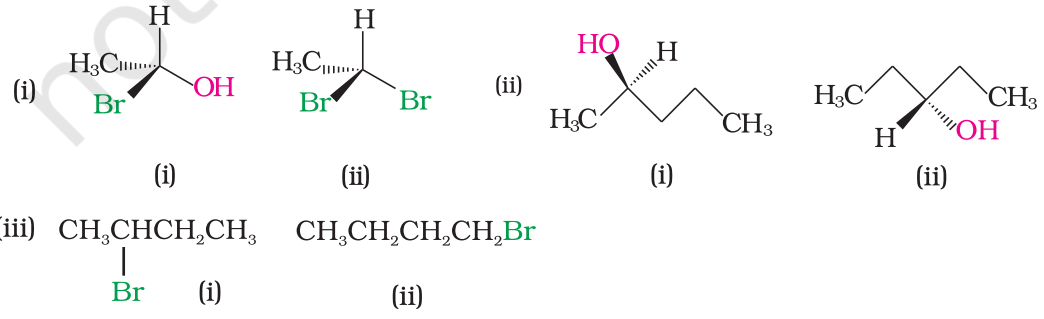
The stereoisomers related to each other as non-superimposable mirror images are called **enantiomers** (Fig. 6.7). A and B in Fig. 6.5 and D and E in Fig. 6.6 are enantiomers.

Enantiomers possess identical physical properties namely, melting point, boiling point, refractive index, etc. They only differ with respect to the rotation of plane polarised light. If one of the enantiomer is *dextro rotatory*, the other will be *laevo rotatory*.

However, the sign of optical rotation is not necessarily related to the absolute (actual) configuration of the molecule.

A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer. Such a mixture is known as **racemic mixture** or **racemic modification**. A racemic mixture is represented by prefixing *dl* or (±) before the name, for example (±) butan-2-ol. The process of conversion of enantiomer into a racemic mixture is known as **racemisation.**

Example 6.8 Identify chiral and achiral molecules in each of the following pair of compounds. (Wedge and Dash representations according to Class XI.



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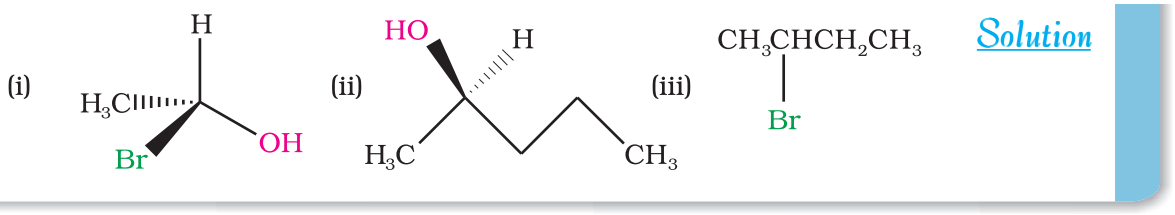
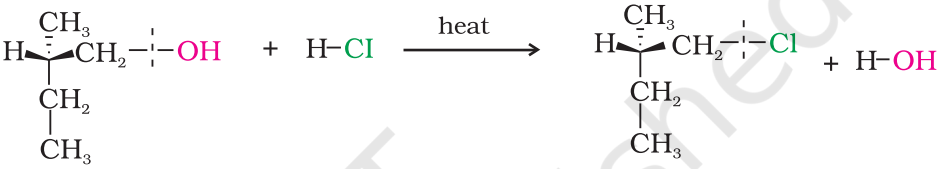


(iii) *Retention:* Retention of configuration is the preservation of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction or transformation.

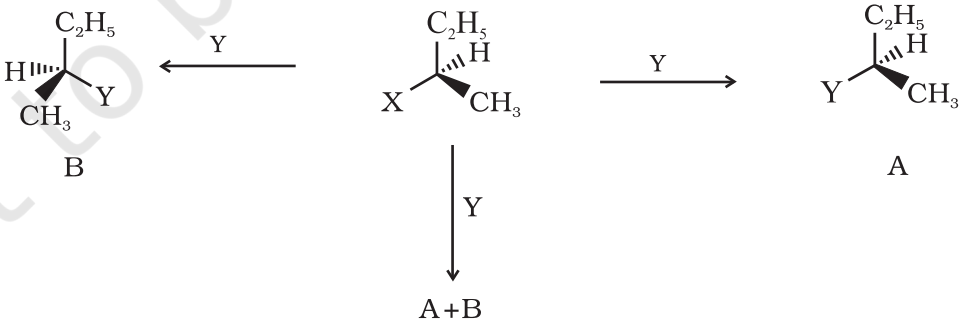
In general, if during a reaction, no bond to the stereocentre is broken, the product will have the same general configuration of groups around the stereocentre as that of reactant. Such a reaction is said to proceed with retention of the configuration. Consider as an example, the reaction that takes place when (–)-2-methylbutan-1-ol is heated with concentrated hydrochloric acid.



(–)–2-Methylbutan-1-ol (+)-1-Chloro-2-methylbutane

It is important to note that configuration at a symmetric centre in the reactant and product is same but the sign of optical rotation has changed in the product. This is so because two different compounds with same configuration at asymmetric centre may have different optical rotation. One may be dextrorotatory (plus sign of optical rotation) while other may be laevorotatory (negative sign of optical rotation).

(iv) *Inversion, retention and racemisation:* There are three outcomes for a reaction at an asymmetric carbon atom, when a bond directly linked to an asymmetric carbon atom is broken. Consider the replacement of a group X by Y in the following reaction;



If (A) is the only compound obtained, the process is called retention of configuration. Note that configuration has been rotated in A.

If (B) is the only compound obtained, the process is called inversion of configuration. Configuration has been inverted in B.

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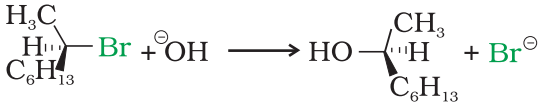
If a 50:50 mixture of A and B is obtained then the process is called racemisation and the product is optically inactive, as one isomer will rotate the plane polarised light in the direction opposite to another.

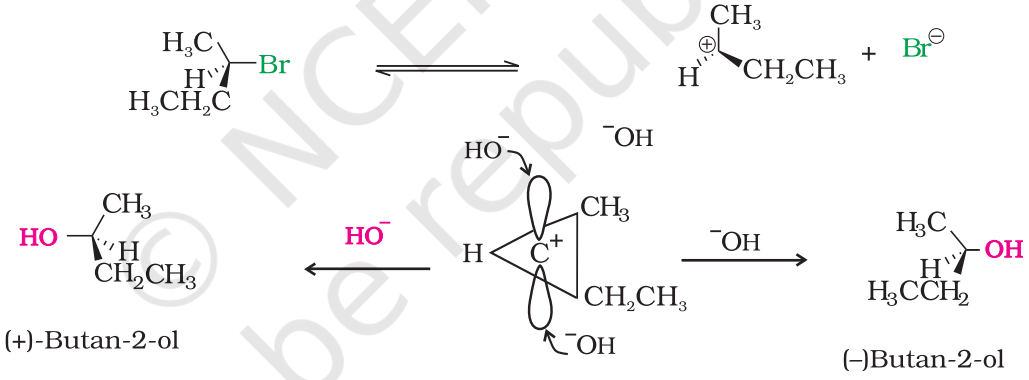
Now let us have a fresh look at S_N1 and S_N2 mechanisms by taking examples of optically active alkyl halides.

In case of optically active alkyl halides, the product formed as a result of S_N2 mechanism has the inverted configuration as compared to the reactant. This is because the nucleophile attaches itself on the side opposite to the one where the halogen atom is present. When (–)-2-bromooctane is allowed to react with sodium hydroxide, (+)-octan-2-ol is formed with the –OH group occupying the position opposite to what bromide had occupied.



Thus, S_N2 reactions of optically active halides are accompanied by inversion of configuration.

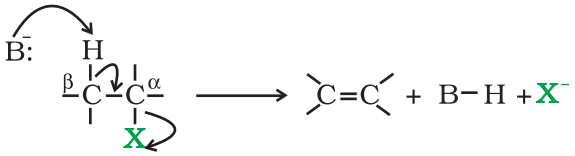
In case of optically active alkyl halides, S_N1 reactions are accompanied by racemisation. Can you think of the reason why it happens? Actually the carbocation formed in the slow step being sp^2 hybridised is planar (achiral). The attack of the nucleophile may be accomplished from either side of the plane of carbocation resulting in a mixture of products, one having the same configuration (the –OH



attaching on the same position as halide ion) and the other having opposite configuration (the –OH attaching on the side opposite to halide ion). This may be illustrated by hydrolysis of optically active 2-bromobutane, which results in the formation of (±)-butan-2-ol.

2. Elimination reactions

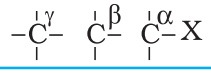
When a haloalkane with β-hydrogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from β-carbon and a halogen atom from the α-carbon atom.



B=Base ; X=Leaving group

Location of α and β carbon in a molecule

Carbon on which halogen atom is directly attached is called α-carbon and the carbon atom adjacent to this carbon is called β-carbon.



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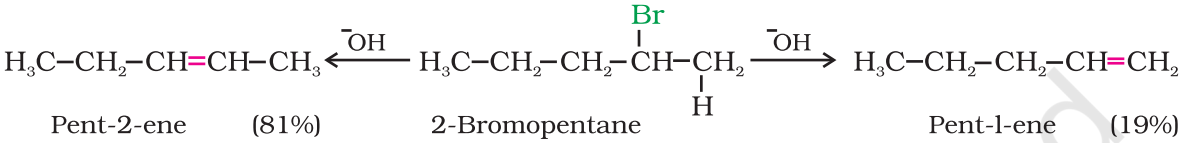
As a result, an alkene is formed as a product. Since β-hydrogen atom is involved in elimination, it is often called **β-elimination**.

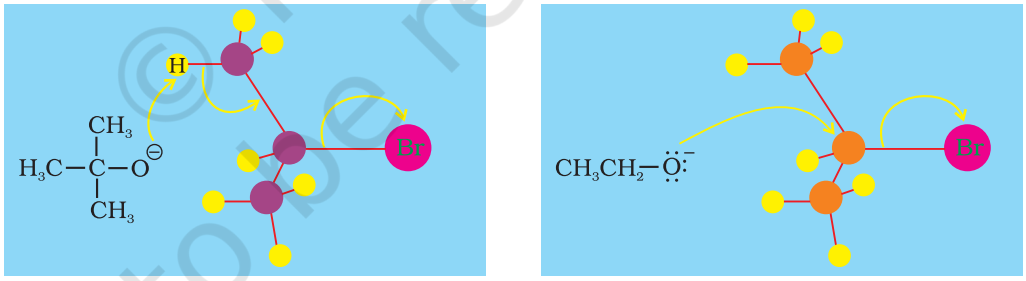
If there is possibility of formation of more than one alkene due to the availability of more than one β-hydrogen atoms, usually one alkene is formed as the major product. These form part of a pattern first observed by Russian chemist, Alexander Zaitsev (also pronounced as Saytzeff) who in 1875 formulated a rule which can be summarised as "*in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.*" Thus, 2-bromopentane gives pent-2-ene as the major product.



Pent-2-ene (81%) 2-Bromopentane Pent-1-ene (19%)

Elimination versus substitution

A chemical reaction is the result of competition; it is a race that is won by the fastest runner. A collection of molecules tend to do, by and large, what is easiest for them. An alkyl halide with β-hydrogen atoms when reacted with a base or a nucleophile has two competing routes: substitution (S_N1 and S_N2) and elimination. Which route will be taken up depends upon the nature of alkyl halide, strength and size of base/nucleophile and reaction conditions. Thus, a bulkier nucleophile will prefer to act as a base and abstracts a proton rather than approach a tetravalent carbon atom (steric reasons) and *vice versa*. Similarly, a primary alkyl halide will prefer a S_N2 reaction, a secondary halide- S_N2 or elimination depending upon the strength of base/nucleophile and a tertiary halide- S_N1 or elimination depending upon the stability of carbocation or the more substituted alkene.



Elimination *vs* Substitution

3. Reaction with metals

Most organic chlorides, bromides and iodides react with certain metals to give compounds containing carbon-metal bonds. Such compounds are known as **organo-metallic compounds**. An important class of organo-metallic compounds discovered by Victor Grignard in 1900 is alkyl magnesium halide, RMgX, referred as **Grignard Reagents**. These reagents are obtained by the reaction of haloalkanes with magnesium metal in dry ether.

$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} CH_3CH_2MgBr$$

Grignard reagent

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Victor Grignard had a strange start in academic life for a chemist - he took a maths degree. When he eventually switched to chemistry, it was not to the mathematical province of physical chemistry but to organic chemistry. While attempting to find an efficient catalyst for the process of methylation, he noted that Zn in diethyl ether had been used for this purpose and wondered whether the Mg/ether combination might be successful. Grignard reagents were first reported in 1900 and Grignard used this work for his doctoral thesis in 1901. In 1910, Grignard obtained a professorship at the University of Nancy and in 1912, he was awarded the Nobel prize for Chemistry which he shared with Paul Sabatier who had made advances in nickel catalysed hydrogenation.

In the Grignard reagent, the carbon-magnesium bond is covalent but highly polar, with carbon pulling electrons from electropositive magnesium; the magnesium halogen bond is essentially ionic.

$$\overset{\delta-}{R}\text{-}\overset{\delta+}{Mg}\,\overset{\delta-}{X}$$

Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons. Even water, alcohols, amines are sufficiently acidic to convert them to corresponding hydrocarbons.

$$RMgX + H_2O \longrightarrow RH + Mg(OH)X$$

It is therefore necessary to avoid even traces of moisture from a Grignard reagent. That is why reaction is carried out in dry ether. On the other hand, this could be considered as one of the methods for converting halides to hydrocarbons.

Wurtz reaction

Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide. This reaction is known as Wurtz reaction.

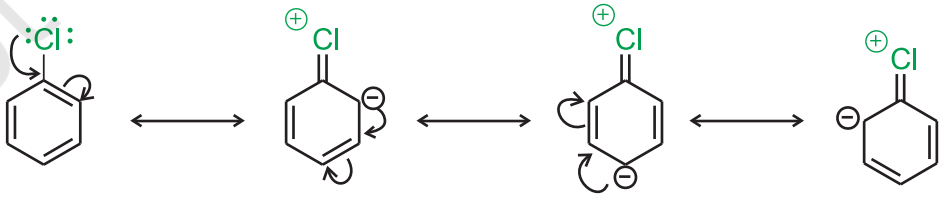
$$2RX + 2Na \longrightarrow RR + 2NaX$$

6.7.2 Reactions of Haloarenes

1. Nucleophilic substitution

Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

(i) *Resonance effect :* In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.



C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

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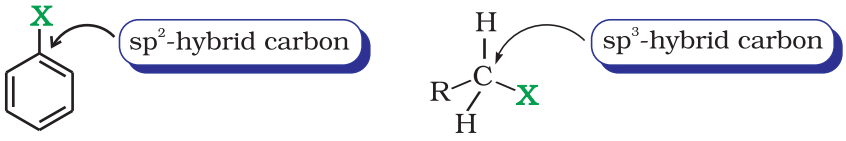
(ii) *Difference in hybridisation of carbon atom in C—X bond:* In haloalkane, the carbon atom attached to halogen is sp^3 hybridised while in case of haloarene, the carbon atom attached to halogen is sp^2-hybridised.



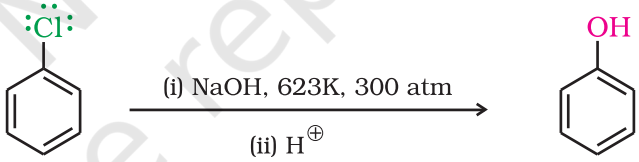
The sp^2 hybridised carbon with a greater *s*-character is more electronegative and can hold the electron pair of C—X bond more tightly than sp^3-hybridised carbon in haloalkane with less *s*-chararcter. Thus, C—Cl bond length in haloalkane is 177pm while in haloarene is 169 pm. Since it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

(iii) *Instability of phenyl cation:* In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, S_N1 mechanism is ruled out.

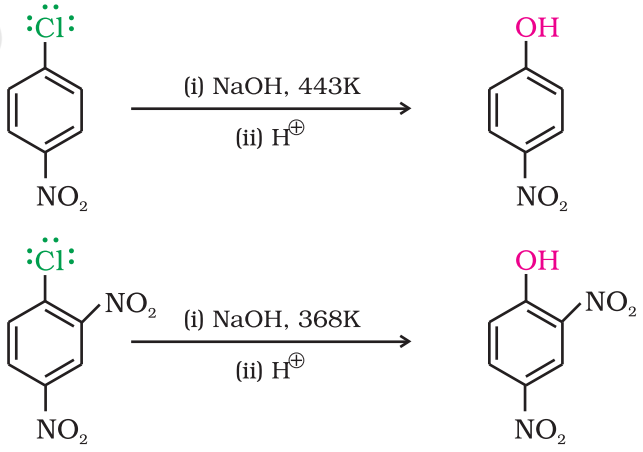
(iv) Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

Replacement by hydroxyl group

Chlorobenzene can be converted into phenol by heating in aqueous sodium hydroxide solution at a temperature of 623K and a pressure of 300 atmospheres.



The presence of an electron withdrawing group (-NO_2) at *ortho*- and *para*-positions increases the reactivity of haloarenes.



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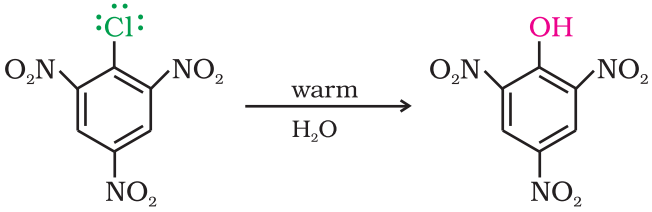
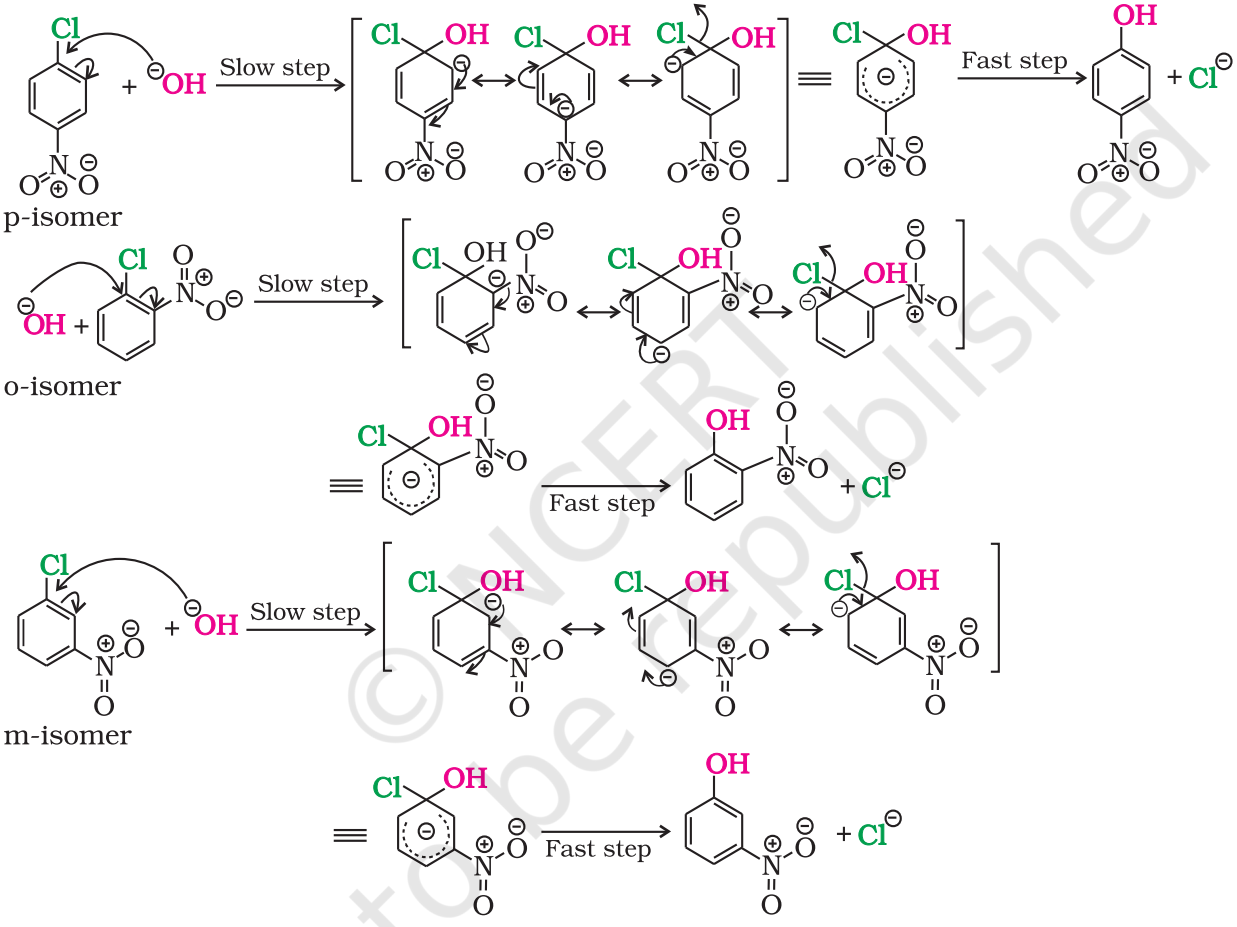


The effect is pronounced when (-NO_2) group is introduced at *ortho-* and *para-* positions. However, no effect on reactivity of haloarenes is observed by the presence of electron withdrawing group at *meta*-position. Mechanism of the reaction is as depicted:



Can you think why does NO_2 group show its effect only at *ortho-* and *para-* positions and not at *meta-* position?

As shown, the presence of nitro group at *ortho-* and *para*-positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene. The carbanion thus formed is stabilised through resonance. The negative charge appeared at *ortho-* and *para-* positions with respect to the halogen substituent is stabilised by $–NO_2$ group while in case of *meta*-nitrobenzene, none of the resonating structures bear the negative charge on carbon atom bearing the $–NO_2$ group. Therefore, the presence of nitro group at *meta-* position does not stabilise the negative charge and no effect on reactivity is observed by the presence of $–NO_2$ group at *meta*-position.

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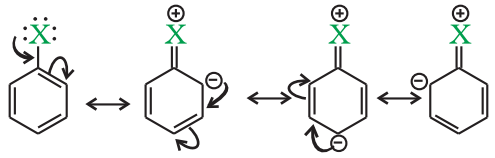
2. Electrophilic substitution reactions

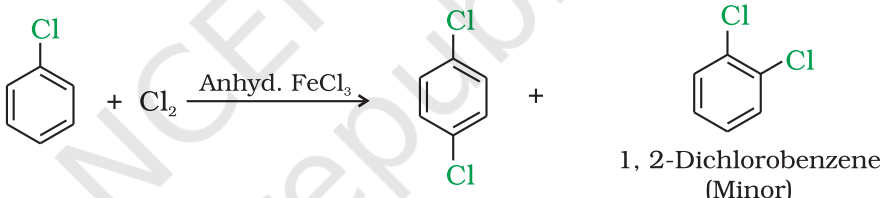
Haloarenes undergo the usual electrophilic reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel-Crafts reactions. Halogen atom besides being slightly deactivating is *o, p*-directing; therefore, further substitution occurs at *ortho*- and *para*-positions with respect to the halogen atom. The *o, p*-directing influence of halogen atom can be easily understood if we consider the resonating structures of halobenzene as shown:



I II III IV

Due to resonance, the electron density increases more at *ortho*- and *para*-positions than at *meta*-positions. Further, the halogen atom because of its –I effect has some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

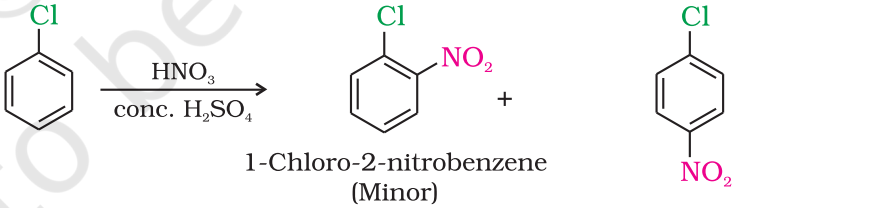
(i) Halogenation



1, 4-Dichlorobenzene (Major)

1, 2-Dichlorobenzene (Minor)

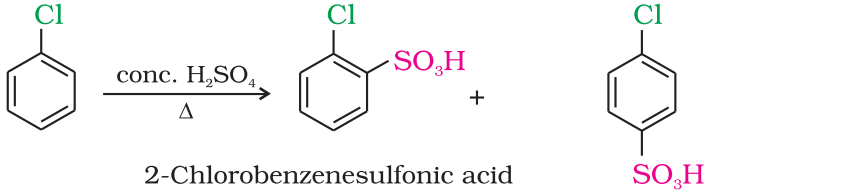
(ii) Nitration



1-Chloro-2-nitrobenzene (Minor)

1-Chloro-4-nitrobenzene (Major)

(iii) Sulphonation



2-Chlorobenzenesulfonic acid (Minor)

4-Chlorobenzenesulfonic acid (Major)

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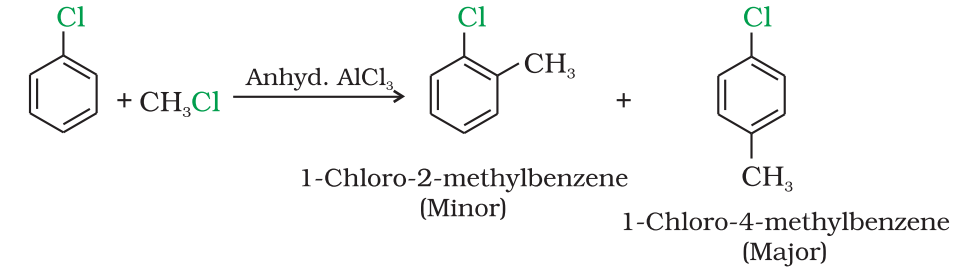
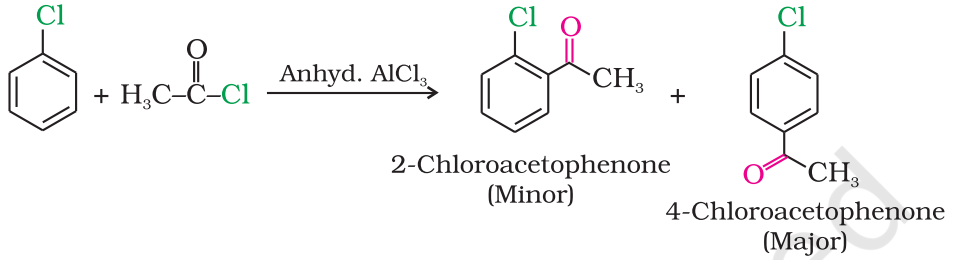
(iv) Friedel-Crafts reaction



1-Chloro-2-methylbenzene (Minor)

1-Chloro-4-methylbenzene (Major)



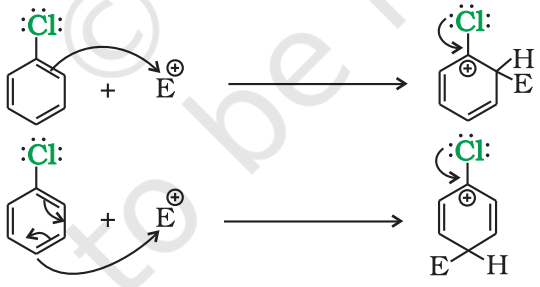
2-Chloroacetophenone (Minor)

4-Chloroacetophenone (Major)

Example 6.9 Although chlorine is an electron withdrawing group, yet it is *ortho-*, *para-* directing in electrophilic aromatic substitution reactions. Why?

Solution Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilises the intermediate carbocation formed during the electrophilic substitution.

Inductive effect destabilises the intermediate carbocation



Resonance effect stabilises the intermediate carbocation

Through resonance, halogen tends to stabilise the carbocation and the effect is more pronounced at *ortho-* and *para-* positions. The inductive effect is stronger than resonance and causes net electron withdrawal and thus causes net deactivation. The resonance effect tends to oppose the inductive effect for the attack at *ortho-* and *para-* positions and hence makes the deactivation less for *ortho-* and *para-* attack. Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect.

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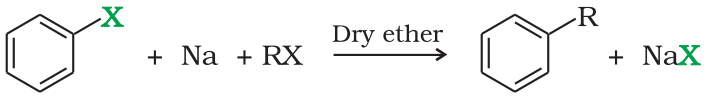
3. Reaction with metals

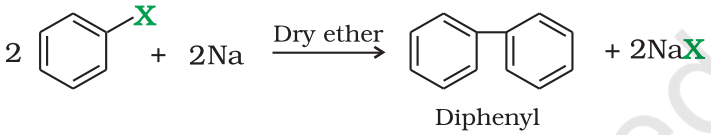
Wurtz-Fittig reaction

A mixture of an alkyl halide and aryl halide gives an alkylarene when treated with sodium in dry ether and is called Wurtz-Fittig reaction.



Fittig reaction

Aryl halides also give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together. It is called Fittig reaction.



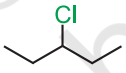
Intext Questions

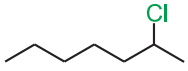
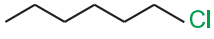
6.7 Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism? Explain your answer.

(i) $CH_3CH_2CH_2CH_2Br$ or $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$ (ii) $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$ or $H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Br$

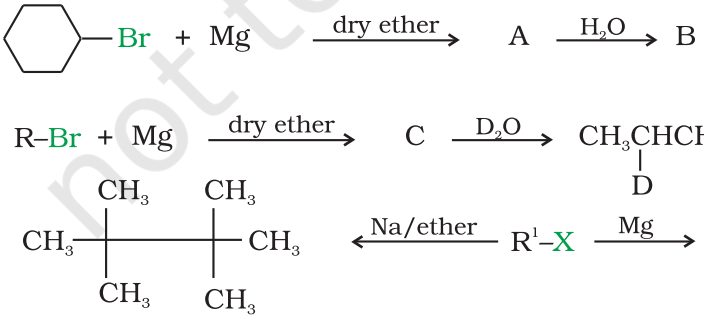
(iii) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2Br$ or $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Br$

6.8 In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

(i) and 

(ii)  and 

6.9 Identify A, B, C, D, E, R and R^1 in the following:



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6.8 Polyhalogen Compounds

Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds. Many of these compounds are useful in industry and agriculture. Some polyhalogen compounds are described in this section.

6.8.1 Dichloromethane (Methylene chloride)

Dichloromethane is widely used as a solvent as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent. Methylene chloride harms the human central nervous system. Exposure to lower levels of methylene chloride in air can lead to slightly impaired hearing and vision. Higher levels of methylene chloride in air cause dizziness, nausea, tingling and numbness in the fingers and toes. In humans, direct skin contact with methylene chloride causes intense burning and mild redness of the skin. Direct contact with the eyes can burn the cornea.

6.8.2 Trichloromethane (Chloroform)

Chemically, chloroform is employed as a solvent for fats, alkaloids, iodine and other substances. The major use of chloroform today is in the production of the freon refrigerant R-22. It was once used as a general anaesthetic in surgery but has been replaced by less toxic, safer anaesthetics, such as ether. As might be expected from its use as an anaesthetic, inhaling chloroform vapours depresses the central nervous system. Breathing about 900 parts of chloroform per million parts of air (900 parts per million) for a short time can cause dizziness, fatigue, and headache. Chronic chloroform exposure may cause damage to the liver (where chloroform is metabolised to phosgene) and to the kidneys, and some people develop sores when the skin is immersed in chloroform. Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene. It is therefore stored in closed dark coloured bottles completely filled so that air is kept out.

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + 2HCl$$

Phosgene

6.8.3 Triiodomethane (Iodoform)

It was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

6.8.4 Tetrachloromethane (Carbon tetrachloride)

It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, pharmaceutical manufacturing, and general solvent use. Until the mid 1960s, it was also widely used as a cleaning fluid, both in industry, as a degreasing agent, and in the home, as a spot remover and as fire extinguisher. There is some evidence that exposure to carbon tetrachloride causes liver cancer in humans. The most common effects are dizziness, light headedness, nausea and vomiting, which can cause permanent damage to nerve cells. In severe cases, these effects can lead rapidly to stupor, coma, unconsciousness or death. Exposure to CCl_4 can make the heart beat irregularly or stop. The chemical may irritate the eyes on contact. When carbon tetrachloride is released into the air, it rises to the atmosphere and depletes the ozone layer. Depletion of the

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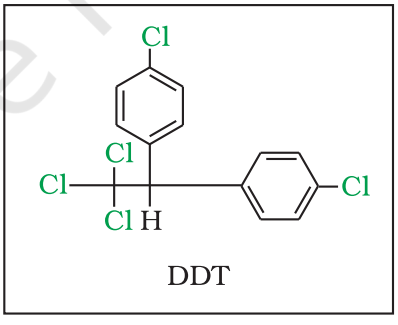
ozone layer is believed to increase human exposure to ultraviolet rays, leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system.

6.8.5 Freons

The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases. Freon 12 (CCl_2F_2) is one of the most common freons in industrial use. It is manufactured from tetrachloromethane by **Swarts reaction.** These are usually produced for aerosol propellants, refrigeration and air conditioning purposes. By 1974, total freon production in the world was about 2 billion pounds annually. Most freon, even that used in refrigeration, eventually makes its way into the atmosphere where it diffuses unchanged into the stratosphere. In stratosphere, freon is able to initiate radical chain reactions that can upset the natural ozone balance.

6.8.6 *p,p'*-Dichlorodiphenyltrichloroethane(DDT)

DDT, the first chlorinated organic insecticides, was originally prepared in 1873, but it was not until 1939 that Paul Muller of Geigy Pharmaceuticals in Switzerland discovered the effectiveness of DDT as an insecticide. Paul Muller was awarded the Nobel Prize in Medicine and Physiology in 1948 for this discovery. The use of DDT increased enormously on a worldwide basis after World War II, primarily because of its effectiveness against the mosquito that spreads malaria and lice that carry typhus. However, problems related to extensive use of DDT began to appear in the late 1940s. Many species of insects developed resistance to DDT, and it was also discovered to have a high toxicity towards fish. The chemical stability of DDT and its fat solubility compounded the problem. DDT is not metabolised very rapidly by animals; instead, it is deposited and stored in the fatty tissues. If ingestion continues at a steady rate, DDT builds up within the animal over time. The use of DDT was banned in the United States in 1973, although it is still in use in some other parts of the world.



DDT

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Summary

Alkyl/ Aryl halides may be classified as mono, di, or polyhalogen (tri-, tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures. Since halogen atoms are more electronegative than carbon, the carbon-halogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge, and the halogen atom bears a partial negative charge.

Alkyl halides are prepared by the **free radical halogenation** of alkanes, addition of halogen acids to alkenes, replacement of –OH group of alcohols with halogens using

phosphorus halides, thionyl chloride or halogen acids. Aryl halides are prepared by **electrophilic substitution** to arenes. Fluorides and iodides are best prepared by halogen exchange method.

The boiling points of organohalogen compounds are comparatively higher than the corresponding hydrocarbons because of strong dipole-dipole and van der Waals forces of attraction. These are slightly soluble in water but completely soluble in organic solvents.

The polarity of carbon-halogen bond of alkyl halides is responsible for their **nucleophilic substitution, elimination** and their reaction with metal atoms to form **organometallic compounds**. Nucleophilic substitution reactions are categorised into S_N1 and S_N2 on the basis of their kinetic properties. **Chirality** has a profound role in understanding the reaction mechanisms of S_N1 and S_N2 reactions. S_N2 reactions of chiral alkyl halides are characterised by the inversion of configuration while S_N1 reactions are characterised by racemisation.

A number of polyhalogen compounds e.g., **dichloromethane**, **chloroform**, **iodoform**, **carbon tetrachloride**, **freon** and **DDT** have many industrial applications. However, some of these compounds cannot be easily decomposed and even cause depletion of ozone layer and are proving **environmental hazards**.

Exercises

6.1 Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides:

(i) $(CH_3)_2CHCH(Cl)CH_3$ (ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$

(iii) $CH_3CH_2C(CH_3)_2CH_2I$ (iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$

(v) $CH_3CH(CH_3)CH(Br)CH_3$ (vi) $CH_3C(C_2H_5)_2CH_2Br$

(vii) $CH_3C(Cl)(C_2H_5)CH_2CH_3$ (viii) $CH_3CH{=}C(Cl)CH_2CH(CH_3)_2$

(ix) $CH_3CH{=}CHC(Br)(CH_3)_2$ (x) *p*-$ClC_6H_4CH_2CH(CH_3)_2$

(xi) *m*-$ClCH_2C_6H_4CH_2C(CH_3)_3$ (xii) *o*-Br-$C_6H_4CH(CH_3)CH_2CH_3$

6.2 Give the IUPAC names of the following compounds:

(i) $CH_3CH(Cl)CH(Br)CH_3$ (ii) $CHF_2CBrClF$ (iii) $ClCH_2C{\equiv}CCH_2Br$

(iv) $(CCl_3)_3CCl$ (v) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$ (vi) $(CH_3)_3CCH{=}CClC_6H_4I\text{-}p$

6.3 Write the structures of the following organic halogen compounds.

(i) 2-Chloro-3-methylpentane (ii) *p*-Bromochlorobenzene

(iii) 1-Chloro-4-ethylcyclohexane (iv) 2-(2-Chlorophenyl)-1-iodooctane

(v) 2-Bromobutane (vi) 4-tert-Butyl-3-iodoheptane

(vii) 1-Bromo-4-sec-butyl-2-methylbenzene (viii) 1,4-Dibromobut-2-ene

6.4 Which one of the following has the highest dipole moment?

(i) CH_2Cl_2 (ii) $CHCl_3$ (iii) CCl_4

6.5 A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

6.6 Write the isomers of the compound having formula C_4H_9Br.

6.7 Write the equations for the preparation of 1-iodobutane from

(i) 1-butanol (ii) 1-chlorobutane (iii) but-1-ene.

6.8 What are ambident nucleophiles? Explain with an example.

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6.9 Which compound in each of the following pairs will react faster in S_N2 reaction with ^-OH?

(i) CH_3Br or CH_3I (ii) $(CH_3)_3CCl$ or CH_3Cl

6.10 Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:

(i) 1-Bromo-1-methylcyclohexane (ii) 2-Chloro-2-methylbutane

(iii) 2,2,3-Trimethyl-3-bromopentane.

6.11 How will you bring about the following conversions?

(i) Ethanol to but-1-yne (ii) Ethane to bromoethene (iii) Propene to 1-nitropropane (iv) Toluene to benzyl alcohol (v) Propene to propyne (vi) Ethanol to ethyl fluoride (vii) Bromomethane to propanone (viii) But-1-ene to but-2-ene (ix) 1-Chlorobutane to n-octane (x) Benzene to biphenyl.

6.12 Explain why

(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

(ii) alkyl halides, though polar, are immiscible with water?

(iii) Grignard reagents should be prepared under anhydrous conditions?

6.13 Give the uses of freon 12, DDT, carbon tetrachloride and iodoform.

6.14 Write the structure of the major organic product in each of the following reactions:

(i) $CH_3CH_2CH_2Cl + NaI \xrightarrow[\text{heat}]{\text{acetone}}$

(ii) $(CH_3)_3CBr + KOH \xrightarrow[\text{heat}]{\text{ethanol}}$

(iii) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{water}}$

(iv) $CH_3CH_2Br + KCN \xrightarrow{\text{aq. ethanol}}$

(v) $C_6H_5ONa + C_2H_5Cl \longrightarrow$

(vi) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$

(vii) $CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{peroxide}}$

(viii) $CH_3CH = C(CH_3)_2 + HBr \longrightarrow$

6.15 Write the mechanism of the following reaction:

$nBuBr + KCN \xrightarrow{EtOH\text{-}H_2O} nBuCN$

6.16 Arrange the compounds of each set in order of reactivity towards S_N2 displacement:

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane

(iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

6.17 Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH.

6.18 *p*-Dichlorobenzene has higher m.p. than those of *o*- and *m*-isomers. Discuss.

6.19 How the following conversions can be carried out?

(i) Propene to propan-1-ol

(ii) Ethanol to but-1-yne

(iii) 1-Bromopropane to 2-bromopropane

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(iv) Toluene to benzyl alcohol
(v) Benzene to 4-bromonitrobenzene
(vi) Benzyl alcohol to 2-phenylethanoic acid
(vii) Ethanol to propanenitrile
(viii) Aniline to chlorobenzene
(ix) 2-Chlorobutane to 3, 4-dimethylhexane
(x) 2-Methyl-1-propene to 2-chloro-2-methylpropane
(xi) Ethyl chloride to propanoic acid
(xii) But-1-ene to n-butyliodide
(xiii) 2-Chloropropane to 1-propanol
(xiv) Isopropyl alcohol to iodoform
(xv) Chlorobenzene to *p*-nitrophenol
(xvi) 2-Bromopropane to 1-bromopropane
(xvii) Chloroethane to butane
(xviii) Benzene to diphenyl
(xix) *tert*-Butyl bromide to isobutyl bromide
(xx) Aniline to phenylisocyanide

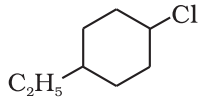
6.20 The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

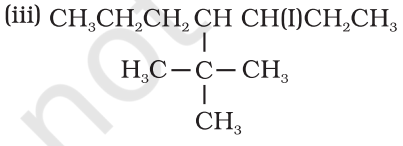
6.21 Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

6.22 What happens when
(i) n-butyl chloride is treated with alcoholic KOH,
(ii) bromobenzene is treated with Mg in the presence of dry ether,
(iii) chlorobenzene is subjected to hydrolysis,
(iv) ethyl chloride is treated with aqueous KOH,
(v) methyl bromide is treated with sodium in the presence of dry ether,
(vi) methyl chloride is treated with KCN?

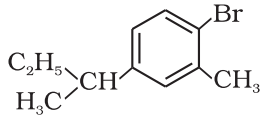
Answers to Some Intext Questions

6.1 (i) $CH_3CH_2CH(CH_3)CHClCH_3$

(ii) 

(iii) 

(iv) $BrCH_2CH = CHCH_2Br$

(v) 

6.2 (i) H_2SO_4 cannot be used along with KI in the conversion of an alcohol to an alkyl iodide as it converts KI to corresponding acid, HI which is then oxidised by it to I_2.

6.3 (i) $ClCH_2CH_2CH_2Cl$ (ii) $ClCH_2CHClCH_3$ (iii) $Cl_2CHCH_2CH_3$ (iv) $CH_3CCl_2CH_3$

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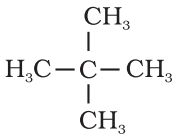
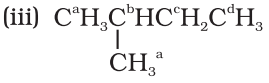
6.4 (i) 

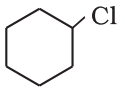
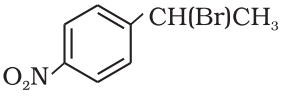
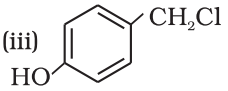
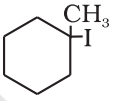
All the hydrogen atoms are equivalent and replacement of any hydrogen will give the same product.

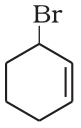
(ii) $C^aH_3C^bH_2C^cH_2C^bH_2C^aH_3$

The equivalent hydrogens are grouped as a, b and c. The replacement of equivalent hydrogens will give the same product.

(iii) 

Similarly the equivalent hydrogens are grouped as a, b, c and d. Thus, four isomeric products are possible.

6.5 (i)  (ii)  (iii)  (iv) 

(v) CH_3CH_2I (vi) 

6.6 (i) Chloromethane, Bromomethane, Dibromomethane, Bromoform. Boiling point increases with increase in molecular mass.

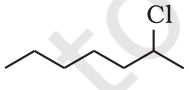
(ii) Isopropylchloride, 1-Chloropropane, 1-Chlorobutane. Isopropylchloride being branched has lower b.p. than 1-Chloropropane.

6.7 (i) $CH_3CH_2CH_2CH_2Br$ Being primary halide, there won't be any steric hindrance.

(ii) Secondary halide reacts faster than tertiary halide.

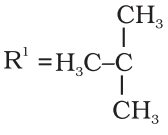
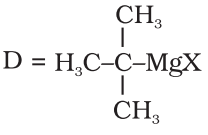
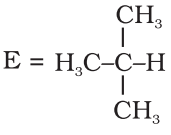
(iii) The presence of methyl group closer to the halide group will increase the steric hindrance and decrease the rate.

6.8 (i) Tertiary halide reacts faster than secondary halide because of the greater stability of tert-carbocation.

(ii)  Because of greater stability of secondary carbocation than primary.

6.9 A = B =

C = RMgBr R =

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Unit

7

Alcohols, Phenols and Ethers

Objectives

After studying this Unit, you will be able to

- name alcohols, phenols and ethers according to the IUPAC system of nomenclature;
- discuss the reactions involved in the preparation of alcohols from alkenes, aldehydes, ketones and carboxylic acids;
- discuss the reactions involved in the preparation of phenols from haloarenes, benzene sulphonic acids, diazonium salts and cumene;
- discuss the reactions for preparation of ethers from (i) alcohols and (ii) alkyl halides and sodium alkoxides/aryloxides;
- correlate physical properties of alcohols, phenols and ethers with their structures;
- discuss chemical reactions of the three classes of compounds on the basis of their functional groups.

Alcohols, phenols and ethers are the basic compounds for the formation of detergents, antiseptics and fragrances, respectively.

You have learnt that substitution of one or more hydrogen atom(s) from a hydrocarbon by another atom or a group of atoms result in the formation of an entirely new compound having altogether different properties and applications. **Alcohols** and **phenols** are formed when a hydrogen atom in a hydrocarbon, aliphatic and aromatic respectively, is replaced by –OH group. These classes of compounds find wide applications in industry as well as in day-to-day life. For instance, have you ever noticed that ordinary spirit used for polishing wooden furniture is chiefly a compound containing hydroxyl group, ethanol. The sugar we eat, the cotton used for fabrics, the paper we use for writing, are all made up of compounds containing –OH groups. Just think of life without paper; no note-books, books, news-papers, currency notes, cheques, certificates, etc. The magazines carrying beautiful photographs and interesting stories would disappear from our life. It would have been really a different world.

An alcohol contains one or more hydroxyl (OH) group(s) directly attached to carbon atom(s), of an aliphatic system (CH_3OH) while a phenol contains –OH group(s) directly attached to carbon atom(s) of an aromatic system (C_6H_5OH).

The substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group (R–O/Ar–O) yields another class of compounds known as 'ethers', for example, CH_3OCH_3 (dimethyl ether). You may also visualise ethers as compounds formed by

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substituting the hydrogen atom of hydroxyl group of an alcohol or phenol by an alkyl or aryl group.

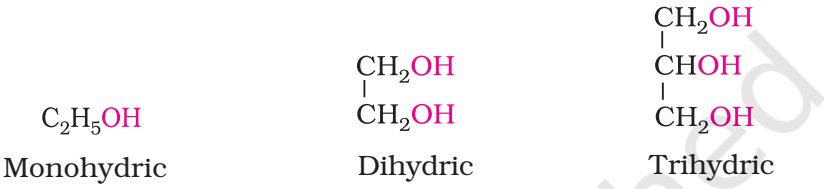
In this unit, we shall discuss the chemistry of three classes of compounds, namely — alcohols, phenols and ethers.

7.1 Classification

The classification of compounds makes their study systematic and hence simpler. Therefore, let us first learn how are alcohols, phenols and ethers classified?

7.1.1 Alcohols—Mono, Di, Tri or Polyhydric alcohols

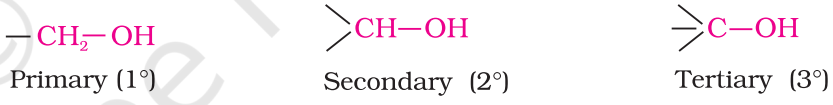
Alcohols and phenols may be classified as mono–, di–, tri- or polyhydric compounds depending on whether they contain one, two, three or many hydroxyl groups respectively in their structures as given below:



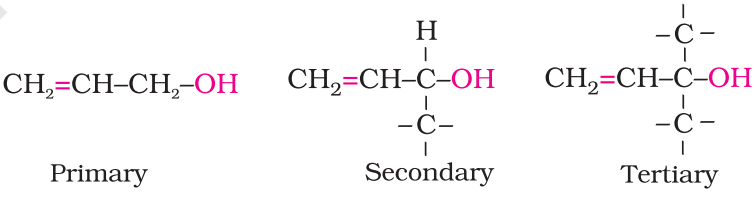
Monohydric alcohols may be further classified according to the hybridisation of the carbon atom to which the hydroxyl group is attached.

(i) Compounds containing $C_{sp^3}-OH$ *bond:* In this class of alcohols, the –OH group is attached to an sp^3 hybridised carbon atom of an alkyl group. They are further classified as follows:

Primary, secondary and tertiary alcohols: In these three types of alcohols, the –OH group is attached to primary, secondary and tertiary carbon atom, respectively as depicted below:



Allylic alcohols: In these alcohols, the —OH group is attached to a sp^3 hybridised carbon adjacent to the carbon-carbon double bond, that is to an allylic carbon. For example



Benzylic alcohols: In these alcohols, the —OH group is attached to a sp^3—hybridised carbon atom next to an aromatic ring. For example.

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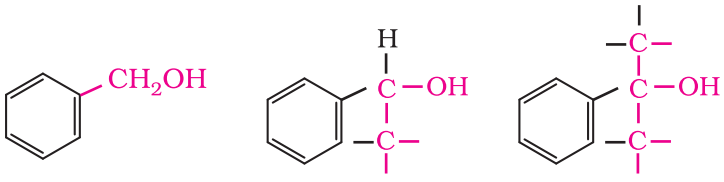


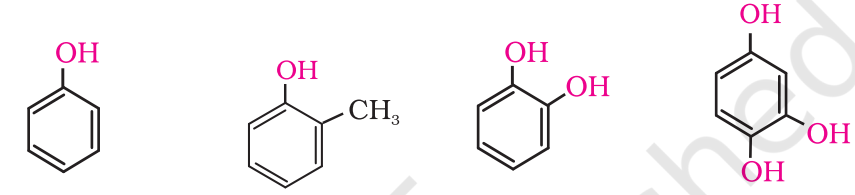
Primary Secondary Tertiary

Allylic and benzylic alcohols may be primary, secondary or tertiary.

(ii) Compounds containing $C_{sp^2}-OH$ *bond:* These alcohols contain —OH group bonded to a carbon-carbon double bond, i.e., to a vinylic carbon or to an aryl carbon. These alcohols are also known as vinylic alcohols.

Vinylic alcohol: $CH_2 = CH - OH$

7.1.2 Phenols—Mono, Di and trihydric phenols



Monohydric Monohydric Dihydric Trihydric

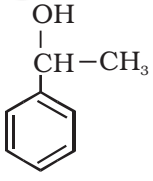
7.1.3 Ethers

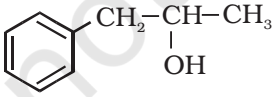
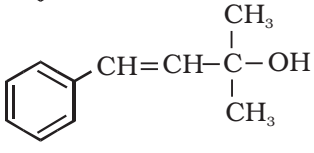
Ethers are classified as **simple** or **symmetrical**, if the alkyl or aryl groups attached to the oxygen atom are the same, and **mixed** or **unsymmetrical**, if the two groups are different. Diethyl ether, $C_2H_5OC_2H_5$, is a symmetrical ether whereas $C_2H_5OCH_3$ and $C_2H_5OC_6H_5$ are unsymmetrical ethers.

Intext Questions

7.1 Classify the following as primary, secondary and tertiary alcohols:

(i) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2OH$ (ii) $H_2C=CH-CH_2OH$

(iii) $CH_3-CH_2-CH_2-OH$ (iv) 

(v)  (vi) 

7.2 Identify allylic alcohols in the above examples.

7.2 Nomenclature

(a) Alcohols: The common name of an alcohol is derived from the common name of the alkyl group and adding the word alcohol to it. For example, CH_3OH is methyl alcohol.

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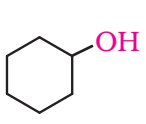
According to IUPAC system, the name of an alcohol is derived from the name of the alkane from which the alcohol is derived, by substituting 'e' of alkane with the suffix 'ol'. The position of substituents are indicated by numerals. For this, the longest carbon chain (parent chain) is numbered starting at the end nearest to the hydroxyl group. The positions of the –OH group and other substituents are indicated by using the numbers of carbon atoms to which these are attached. For naming polyhydric alcohols, the 'e' of alkane is retained and the ending 'ol' is added. The number of –OH groups is indicated by adding the multiplicative prefix, di, tri, etc., before 'ol'. The positions of –OH groups are indicated by appropriate locants, e.g., HO–CH_2–CH_2–OH is named as ethane–1, 2-diol. Table 7.1 gives common and IUPAC names of a few alcohols as examples.

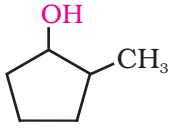
Table 7.1: Common and IUPAC Names of Some Alcohols

Compound	Common name	IUPAC name
$CH_3 - OH$	Methyl alcohol	Methanol
$CH_3 - CH_2 - CH_2 - OH$	*n*-Propyl alcohol	Propan-1-ol
$CH_3 - \underset{\displaystyle OH}{\underset{\vert}{CH}} - CH_3$	Isopropyl alcohol	Propan-2-ol
$CH_3 - CH_2 - CH_2 - CH_2 - OH$	*n*-Butyl alcohol	Butan-1-ol
$CH_3 - \underset{\displaystyle OH}{\underset{\vert}{CH}} - CH_2 - CH_3$	*sec*-Butyl alcohol	Butan-2-ol
$CH_3 - \underset{\displaystyle CH_3}{\underset{\vert}{CH}} - CH_2 - OH$	Isobutyl alcohol	2-Methylpropan-1-ol
$CH_3 - \underset{\displaystyle CH_3}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}} - OH$	*tert*-Butyl alcohol	2-Methylpropan-2-ol
$HO-H_2C-CH_2-OH$	Ethylene glycol	Ethane-1,2-diol
$\underset{\displaystyle OH}{\underset{\vert}{CH_2}} - \underset{\displaystyle OH}{\underset{\vert}{CH}} - \underset{\displaystyle OH}{\underset{\vert}{CH_2}}$	Glycerol	Propane -1, 2, 3-triol

Cyclic alcohols are named using the prefix cyclo and considering the —OH group attached to C–1.



Cyclohexanol



2-Methylcyclopentanol

(b) Phenols: The simplest hydroxy derivative of benzene is phenol. It is its common name and also an accepted IUPAC name. As structure of phenol involves a benzene ring, in its substituted compounds the terms *ortho* (1,2- disubstituted), *meta* (1,3-disubstituted) and *para* (1,4-disubstituted) are often used in the common names.

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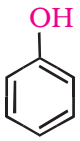
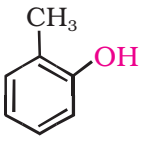
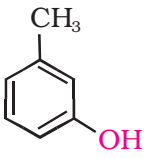
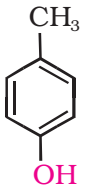
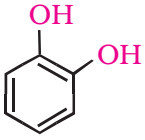
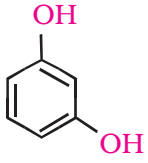
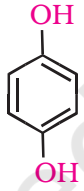
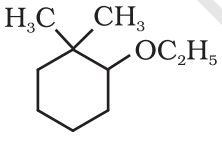
				
Common name	Phenol	*o*-Cresol	*m*-Cresol	*p*-Cresol
IUPAC name	Phenol	2-Methylphenol	3-Methylphenol	4-Methylphenol

Dihydroxy derivatives of benzene are known as 1, 2-, 1, 3- and 1, 4-benzenediol.

			
Common name	Catechol	Resorcinol	Hydroquinone or quinol
IUPAC name	Benzene-1,2-diol	Benzene-1,3-diol	Benzene-1,4-diol

(c) Ethers: Common names of ethers are derived from the names of alkyl/aryl groups written as separate words in alphabetical order and adding the word 'ether' at the end. For example, $CH_3OC_2H_5$ is ethylmethyl ether.

Table 7.2: Common and IUPAC Names of Some Ethers

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$CH_3OCH_2CH_2CH_3$	Methyl n-propyl ether	1-Methoxypropane
$C_6H_5OCH_3$	Methyl phenyl ether (Anisole)	Methoxybenzene (Anisole)
$C_6H_5OCH_2CH_3$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$C_6H_5O(CH_2)_6-CH_3$	Heptyl phenyl ether	1-Phenoxyheptane
$CH_3O-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH_3$	Methyl isopropyl ether	2-Methoxypropane
$C_6H_5-O-CH_2-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH_3$	Phenyl isopentyl ether	3- Methylbutoxybenzene
$CH_3-O-CH_2-CH_2-OCH_3$	—	1,2-Dimethoxyethane
	—	2-Ethoxy- -1,1-dimethylcyclohexane

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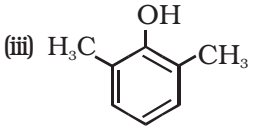
If both the alkyl groups are the same, the prefix 'di' is added before the alkyl group. For example, $C_2H_5OC_2H_5$ is diethyl ether.

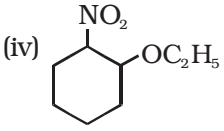
According to IUPAC system of nomenclature, ethers are regarded as hydrocarbon derivatives in which a hydrogen atom is replaced by an –OR or –OAr group, where R and Ar represent alkyl and aryl groups, respectively. The larger (R) group is chosen as the parent hydrocarbon. The names of a few ethers are given as examples in Table 7.2.

Example 7.1 Give IUPAC names of the following compounds:

(i) $CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

(ii) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-CH_2CH_3$

(iii) 

(iv) 

Solution (i) 4-Chloro-2,3-dimethylpentan-1-ol (ii) 2-Ethoxypropane

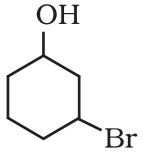
(iii) 2,6-Dimethylphenol (iv) 1-Ethoxy-2-nitrocyclohexane

Intext Question

7.3 Name the following compounds according to IUPAC system.

(i) $CH_3-CH_2-\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}-\underset{}{\overset{\displaystyle CH_2OH}{\overset{|}{CH}}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(ii) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-\overset{\displaystyle CH_2OH}{\overset{|}{CH}}-CH_3$

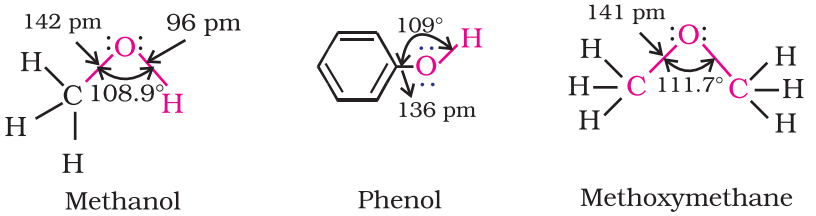
(iii) 

(iv) $H_2C=CH-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_2-CH_3$

(v) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=\underset{\displaystyle Br}{\underset{|}{C}}-CH_2OH$

7.3 Structures of Functional Groups

In alcohols, the oxygen of the –OH group is attached to carbon by a sigma (σ) bond formed by the overlap of a sp^3 hybridised orbital of carbon with a sp^3 hybridised orbital of oxygen. Fig. 7.1 depicts structural aspects of methanol, phenol and methoxymethane.



Methanol Phenol Methoxymethane

Fig. 7.1: Structures of methanol, phenol and methoxymethane

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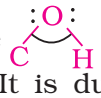
The bond angle  in alcohols is slightly less than the tetrahedral angle (109°-28′). It is due to the repulsion between the unshared electron pairs of oxygen. In phenols, the –OH group is attached to sp^2 hybridised carbon of an aromatic ring. The carbon– oxygen bond length (136 pm) in phenol is slightly less than that in methanol. This is due to (i) partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring (Section 7.4.4) and (ii) sp^2 hybridised state of carbon to which oxygen is attached.

In ethers, the four electron pairs, i.e., the two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in a tetrahedral arrangement. The bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky (–R) groups. The C–O bond length (141 pm) is almost the same as in alcohols.

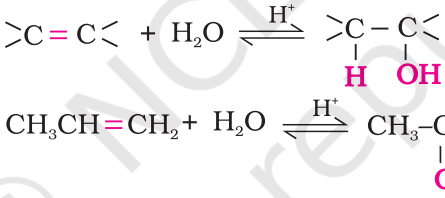
7.4 Alcohols and Phenols

7.4.1 Preparation of Alcohols

Alcohols are prepared by the following methods:

1. From alkenes

(i) *By acid catalysed hydration:* Alkenes react with water in the presence of acid as catalyst to form alcohols. In case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markovnikov's rule.

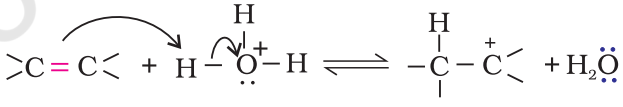


Mechanism

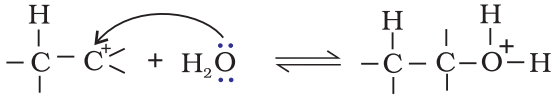
The mechanism of the reaction involves the following three steps:

Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

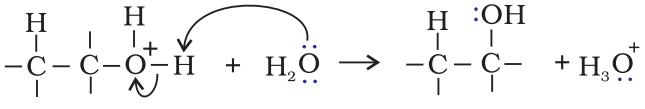
$$H_2O + H^+ \rightarrow H_3O^+$$



Step 2: Nucleophilic attack of water on carbocation.



Step 3: Deprotonation to form an alcohol.



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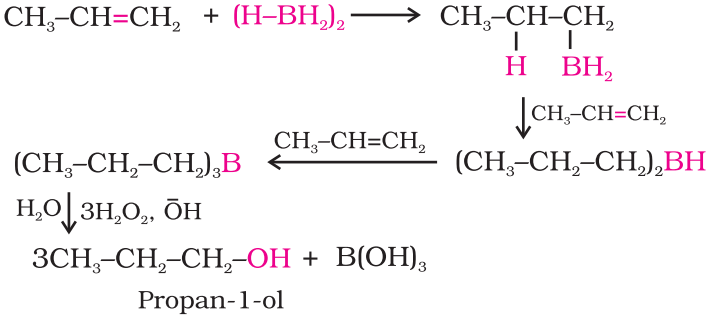
Hydroboration - oxidation was first reported by H.C. Brown in 1959. For his studies on boron containing organic compounds, Brown shared the 1979 Nobel prize in Chemistry with G. Wittig.

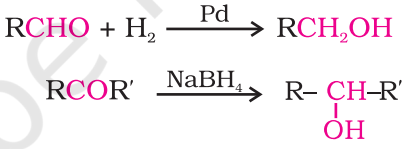
(ii) *By hydroboration–oxidation*: Diborane $(BH_3)_2$ reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



The addition of borane to the double bond takes place in such a manner that the boron atom gets attached to the sp^2 carbon carrying greater number of hydrogen atoms. The alcohol so formed looks as if it has been formed by the addition of water to the alkene in a way opposite to the Markovnikov's rule. In this reaction, alcohol is obtained in excellent yield.

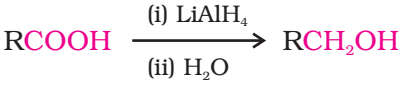
2. From carbonyl compounds

(i) *By reduction of aldehydes and ketones*: Aldehydes and ketones are reduced to the corresponding alcohols by addition of hydrogen in the presence of catalysts (catalytic hydrogenation). The usual catalyst is a finely divided metal such as platinum, palladium or nickel. It is also prepared by treating aldehydes and ketones with sodium borohydride ($NaBH_4$) or lithium aluminium hydride ($LiAlH_4$). Aldehydes yield primary alcohols whereas ketones give secondary alcohols.



The numbers in front of the reagents along the arrow indicate that the second reagent is added only when the reaction with first is complete.

(ii) *By reduction of carboxylic acids and esters*: Carboxylic acids are reduced to primary alcohols in excellent yields by lithium aluminium hydride, a strong reducing agent.



However, $LiAlH_4$ is an expensive reagent, and therefore, used for preparing special chemicals only. Commercially, acids are reduced to alcohols by converting them to the esters (Section 7.4.4), followed by their reduction using hydrogen in the presence of catalyst (catalytic hydrogenation).

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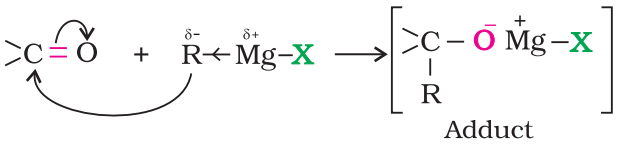
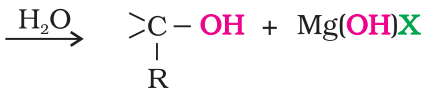
3. From Grignard reagents

Alcohols are produced by the reaction of Grignard reagents (Unit 6, Class XII) with aldehydes and ketones.

The first step of the reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct. Hydrolysis of the adduct yields an alcohol.



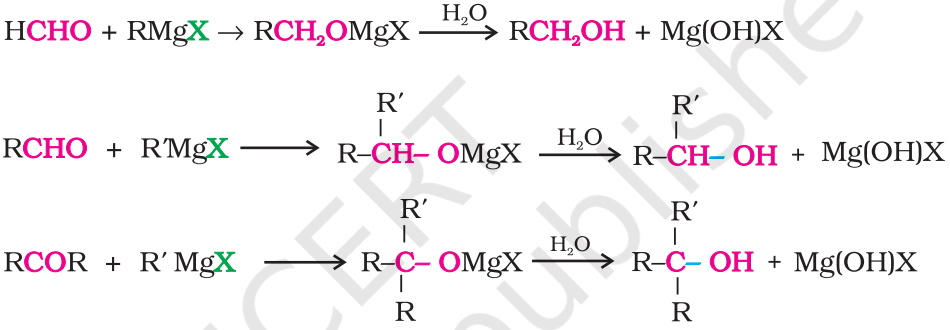
... (i)



...(ii)

The reaction of Grignard reagents with methanal produces a primary alcohol, with other aldehydes, secondary alcohols and with ketones, tertiary alcohols.

The overall reactions using different aldehydes and ketones are as follows:



You will notice that the reaction produces a primary alcohol with methanal, a secondary alcohol with other aldehydes and tertiary alcohol with ketones.

Example 7.2

Give the structures and IUPAC names of the products expected from the following reactions:

(a) Catalytic reduction of butanal.

(b) Hydration of propene in the presence of dilute sulphuric acid.

(c) Reaction of propanone with methylmagnesium bromide followed by hydrolysis.

Solution

(a) $CH_3–CH_2–CH_2–CH_2–OH$ Butan-1-ol

(b) $CH_3–\underset{\displaystyle OH}{\underset{|}{CH}}–CH_3$ Propan-2-ol

(c) $CH_3–\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}–OH$ 2-Methylpropan-2-ol

7.4.2 Preparation of Phenols

Phenol, also known as carbolic acid, was first isolated in the early nineteenth century from coal tar. Nowadays, phenol is commercially produced synthetically. In the laboratory, phenols are prepared from benzene derivatives by any of the following methods:

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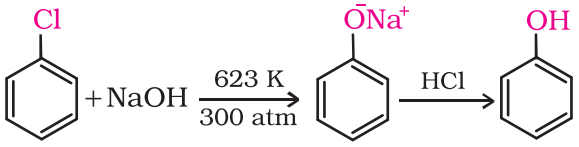
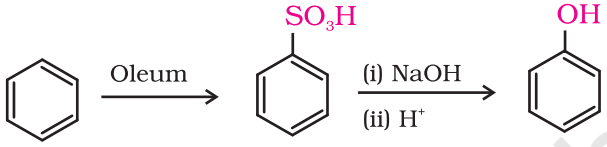
1. *From haloarenes*

Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by acidification of sodium phenoxide so produced (Unit 6, Class XII).



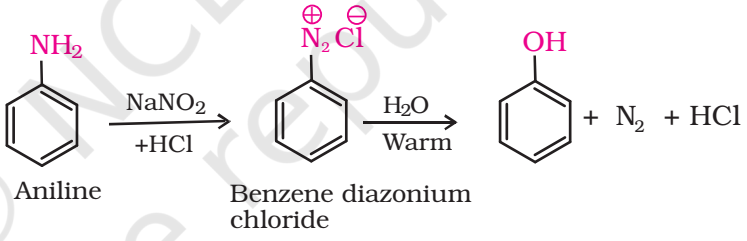
2. *From benzenesulphonic acid*

Benzene is sulphonated with oleum and benzene sulphonic acid so formed is converted to sodium phenoxide on heating with molten sodium hydroxide. Acidification of the sodium salt gives phenol.



3. *From diazonium salts*

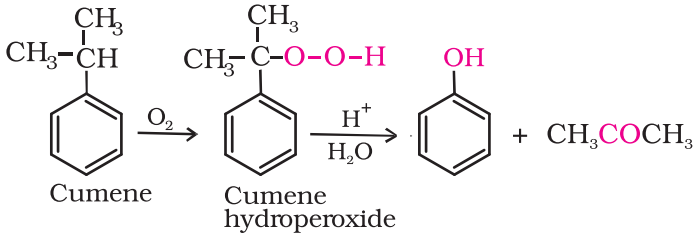
A diazonium salt is formed by treating an aromatic primary amine with nitrous acid ($NaNO_2$ + HCl) at 273-278 K. Diazonium salts are hydrolysed to phenols by warming with water or by treating with dilute acids (Unit 9, Class XII).



Most of the worldwide production of phenol is from cumene.

4. *From cumene*

Phenol is manufactured from the hydrocarbon, cumene. Cumene (isopropylbenzene) is oxidised in the presence of air to cumene hydroperoxide. It is converted to phenol and acetone by treating it with dilute acid. Acetone, a by-product of this reaction, is also obtained in large quantities by this method.



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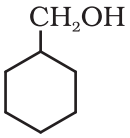
Intext Questions

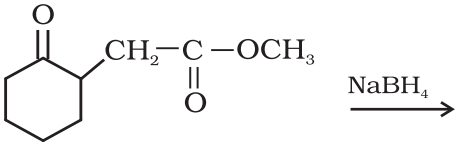
7.4 Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal ?

(i) $CH_3–\underset{\displaystyle CH_3}{\underset{|}{CH}}–CH_2OH$

(ii) 

7.5 Write structures of the products of the following reactions:

(i) $CH_3 - CH = CH_2 \xrightarrow{H_2O/H^+}$

(ii) 

(iii) $CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CHO \xrightarrow{NaBH_4}$

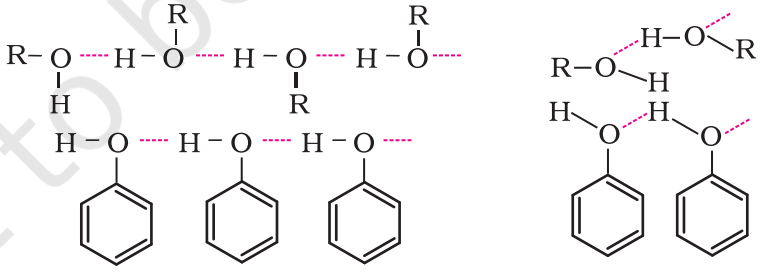
7.4.3 Physical Properties

Alcohols and phenols consist of two parts, an alkyl/aryl group and a hydroxyl group. The properties of alcohols and phenols are chiefly due to the hydroxyl group. The nature of alkyl and aryl groups simply modify these properties.

Boiling Points

The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area).

The –OH group in alcohols and phenols is involved in intermolecular hydrogen bonding as shown below:



It is interesting to note that boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. For example, ethanol and propane have comparable molecular masses but their boiling points differ widely. The boiling point of methoxymethane is intermediate of the two boiling points.

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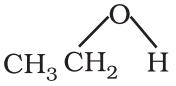
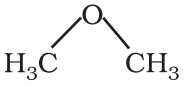
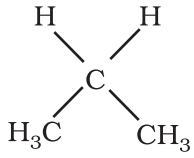


Ethanol
Molecular mass/b.p.
46/ 351 K



Methoxymethane
Molecular mass/b.p.
46/248 K

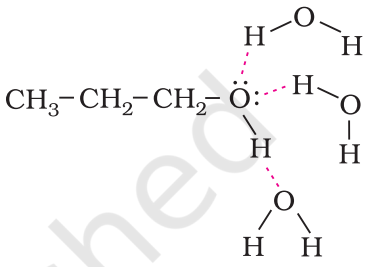


Propane
Molecular mass/b.p.
44/231 K

The high boiling points of alcohols are mainly due to the presence of intermolecular hydrogen bonding in them which is lacking in ethers and hydrocarbons.

Solubility

Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules as shown. The solubility decreases with increase in size of alkyl/aryl (hydrophobic) groups. Several of the lower molecular mass alcohols are miscible with water in all proportions.



Example 7.3 Arrange the following sets of compounds in order of their increasing boiling points:

(a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.

(b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.

Solution

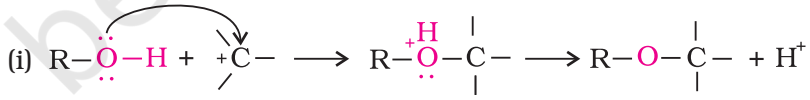
(a) Methanol, ethanol, propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol.

(b) n-Butane, ethoxyethane, pentanal and pentan-1-ol.

7.4.4 Chemical Reactions

Alcohols are versatile compounds. They react both as nucleophiles and electrophiles. The bond between O–H is broken when alcohols react as nucleophiles.

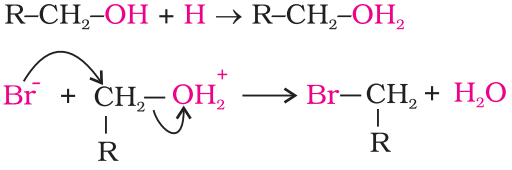
Alcohols as nucleophiles



(i) $R-\ddot{O}-H + \overset{+}{C}- \longrightarrow R-\overset{+}{\underset{\cdot\cdot}{O}}(H)-C- \longrightarrow R-O-C- + H^+$

(ii) The bond between C–O is broken when they react as electrophiles. Protonated alcohols react in this manner.

Protonated alcohols as electrophiles



$R-CH_2-OH + \overset{+}{H} \rightarrow R-CH_2-\overset{+}{O}H_2$

$Br^- + CH_2(R)-\overset{+}{O}H_2 \longrightarrow Br-CH_2(R) + H_2O$

Based on the cleavage of O–H and C–O bonds, the reactions of alcohols and phenols may be divided into two groups:

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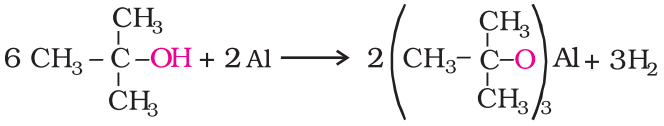
(a) Reactions involving cleavage of O–H bond

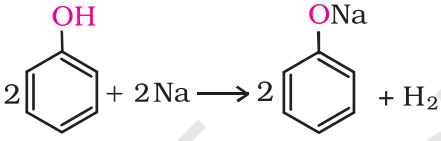
1. *Acidity of alcohols and phenols*

(i) Reaction with metals: Alcohols and phenols react with active metals such as sodium, potassium and aluminium to yield corresponding alkoxides/phenoxides and hydrogen.

$$2R{-}O{-}H + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2R{-}O{-}Na} + H_2$$

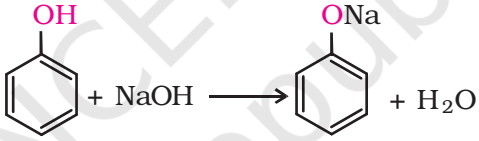


tert- Butyl alcohol — Aluminium *tert*- butoxide



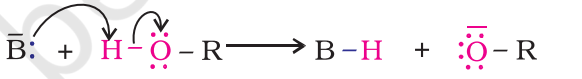
Phenol — Sodium phenoxide

In addition to this, phenols react with aqueous sodium hydroxide to form sodium phenoxides.



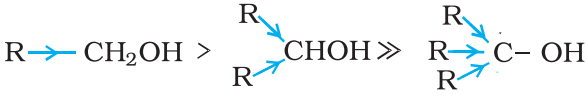
Sodium phenoxide

The above reactions show that alcohols and phenols are acidic in nature. In fact, alcohols and phenols are Brönsted acids i.e., they can donate a proton to a stronger base (B:).



Base — Acid — Conjugate acid — Conjugate base

(ii) Acidity of alcohols: The acidic character of alcohols is due to the polar nature of O–H bond. An electron-releasing group ($-CH_3$, $-C_2H_5$) increases electron density on oxygen tending to decrease the polarity of O-H bond. This decreases the acid strength. For this reason, the acid strength of alcohols decreases in the following order:



Primary — Secondary — Tertiary

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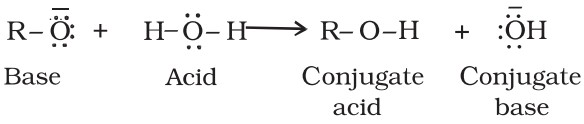
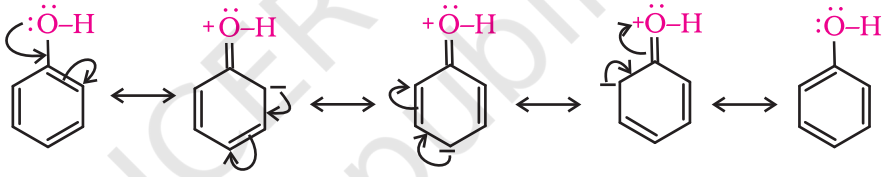
Alcohols are, however, weaker acids than water. This can be illustrated by the reaction of water with an alkoxide.



This reaction shows that water is a better proton donor (i.e., stronger acid) than alcohol. Also, in the above reaction, we note that an alkoxide ion is a better proton acceptor than hydroxide ion, which suggests that alkoxides are stronger bases (sodium ethoxide is a stronger base than sodium hydroxide).

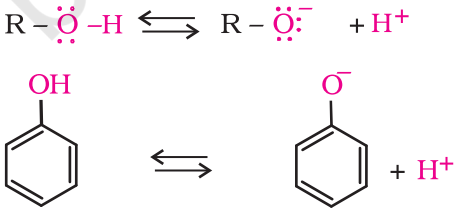
Alcohols act as Bronsted bases as well. It is due to the presence of unshared electron pairs on oxygen, which makes them proton acceptors.

(iii) Acidity of phenols: The reactions of phenol with metals (e.g., sodium, aluminium) and sodium hydroxide indicate its acidic nature. The hydroxyl group, in phenol is directly attached to the sp^2 hybridised carbon of benzene ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule, as depicted in its resonance structures, causes the oxygen of –OH group to be positive.



The reaction of phenol with aqueous sodium hydroxide indicates that phenols are stronger acids than alcohols and water. Let us examine how a compound in which hydroxyl group attached to an aromatic ring is more acidic than the one in which hydroxyl group is attached to an alkyl group.

The ionisation of an alcohol and a phenol takes place as follows:



Due to the higher electronegativity of sp^2 hybridised carbon of phenol to which –OH is attached, electron density decreases on oxygen. This increases the polarity of O–H bond and results in an increase in ionisation of phenols than that of alcohols. Now let us examine the stabilities of alkoxide and phenoxide ions. In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalisation of negative charge (structures I-V) makes

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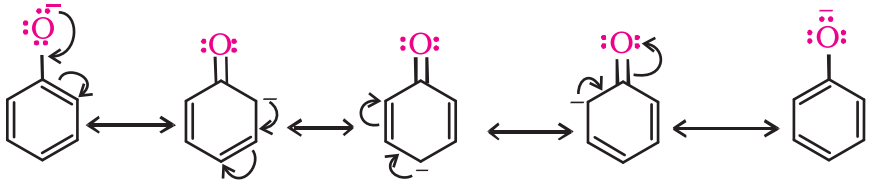
phenoxide ion more stable and favours the ionisation of phenol. Although there is also charge delocalisation in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than phenoxide ion.



I II III IV V

In substituted phenols, the presence of electron withdrawing groups such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para* positions. It is due to the effective delocalisation of negative charge in phenoxide ion when substituent is at ortho or para position. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic than phenol.

The greater the pK_a *value, the weaker the acid.*

Table 7.3: pK_a Values of some Phenols and Ethanol

Compound	Formula	pK_a
o-Nitrophenol	*o*-O_2N–C_6H_4–OH	7.2
m-Nitrophenol	*m*–O_2N–C_6H_4–OH	8.3
p-Nitrophenol	*p*-O_2N–C_6H_4–OH	7.1
Phenol	C_6H_5–OH	10.0
o-Cresol	*o*-CH_3–C_6H_4–OH	10.2
m-Cresol	*m*-$CH_3C_6H_4$–OH	10.1
p-Cresol	*p*-CH_3–C_6H_4–OH	10.2
Ethanol	C_2H_5OH	15.9

From the above data, you will note that phenol is million times more acidic than ethanol.

Example 7.4

Arrange the following compounds in increasing order of their acid strength: Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol.

Solution

Propan-1-ol, 4-methylphenol, phenol, 3-nitrophenol, 3,5-dinitrophenol, 2,4, 6-trinitrophenol.

2. *Esterification*

Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.

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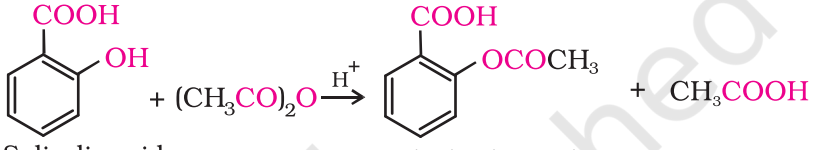
$$Ar/ROH + R'-COOH \underset{}{\overset{H^+}{\rightleftharpoons}} Ar/ROCOR' + H_2O$$

$$Ar/R-OH + (R'CO)_2O \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + R'COOH$$

$$R/ArOH + R'COCl \xrightarrow{\text{Pyridine}} R/ArOCOR' + HCl$$

Aspirin possesses analgesic, anti-inflammatory and antipyretic properties.

The reaction with carboxylic acid and acid anhydride is carried out in the presence of a small amount of concentrated sulphuric acid. The reaction is reversible, and therefore, water is removed as soon as it is formed. The reaction with acid chloride is carried out in the presence of a base (pyridine) so as to neutralise HCl which is formed during the reaction. It shifts the equilibrium to the right hand side. The introduction of acetyl (CH_3CO) group in alcohols or phenols is known as acetylation. Acetylation of salicylic acid produces aspirin.



Salicylic acid — Acetylsalicylic acid (Aspirin)

(b) Reactions involving cleavage of carbon – oxygen (C–O) bond in alcohols

The reactions involving cleavage of C–O bond take place only in alcohols. Phenols show this type of reaction only with zinc.

1. ***Reaction with hydrogen halides:*** Alcohols react with hydrogen halides to form alkyl halides (Refer Unit 6, Class XII).

$$ROH + HX \rightarrow R-X + H_2O$$

The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another (**Lucas test**). Alcohols are soluble in Lucas reagent (conc. HCl and $ZnCl_2$) while their halides are immiscible and produce turbidity in solution. In case of tertiary alcohols, turbidity is produced immediately as they form the halides easily. Primary alcohols do not produce turbidity at room temperature.

2. ***Reaction with phosphorus trihalides:*** Alcohols are converted to alkyl bromides by reaction with phosphorus tribromide (Refer Unit 6, Class XII).

3. ***Dehydration:*** Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with a protic acid e.g., concentrated H_2SO_4 or H_3PO_4, or catalysts such as anhydrous zinc chloride or alumina.

$$-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OH}{C}}- \xrightarrow[\text{Heat}]{H^+} >C=C< + H_2O$$

Ethanol undergoes dehydration by heating it with concentrated H_2SO_4 at 443 K.

$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O$$

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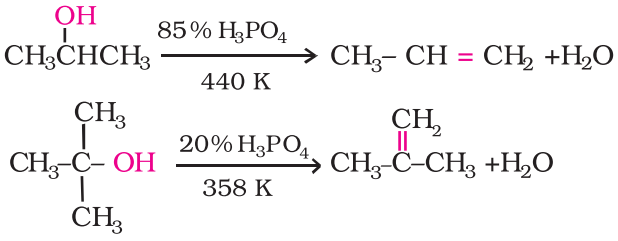
Secondary and tertiary alcohols are dehydrated under milder conditions. For example



Thus, the relative ease of dehydration of alcohols follows the following order:

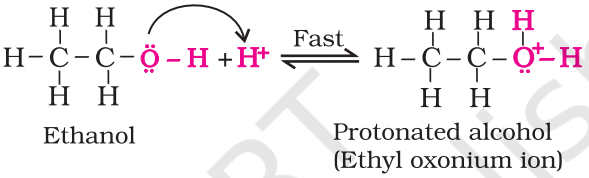
Tertiary > Secondary > Primary

The mechanism of dehydration of ethanol involves the following steps:

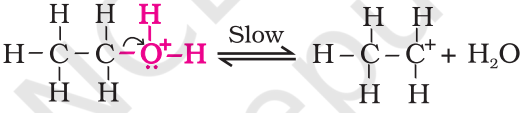
Tertiary carbocations are more stable and therefore are easier to form than secondary and primary carbocations; tertiary alcohols are the easiest to dehydrate.

Mechanism

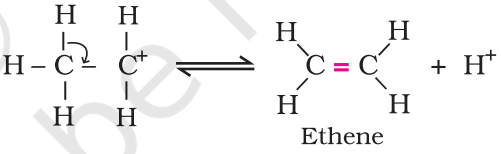
Step 1: Formation of protonated alcohol.



Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.

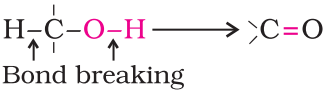


Step 3: Formation of ethene by elimination of a proton.



The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

4. *Oxidation:* Oxidation of alcohols involves the formation of a carbon-oxygen double bond with cleavage of an O-H and C-H bonds.



Such a cleavage and formation of bonds occur in oxidation reactions. These are also known as **dehydrogenation** reactions as these involve loss of dihydrogen from an alcohol molecule. Depending on the oxidising agent used, a primary alcohol is oxidised to an aldehyde which in turn is oxidised to a carboxylic acid.

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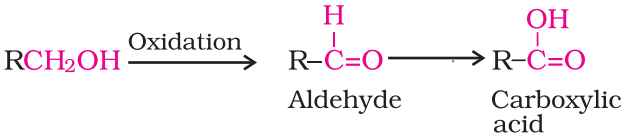


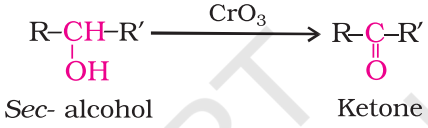
Strong oxidising agents such as acidified potassium permanganate are used for getting carboxylic acids from alcohols directly. CrO_3 in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.

$$RCH_2OH \xrightarrow{CrO_3} RCHO$$

A better reagent for oxidation of primary alcohols to aldehydes in good yield is pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl.

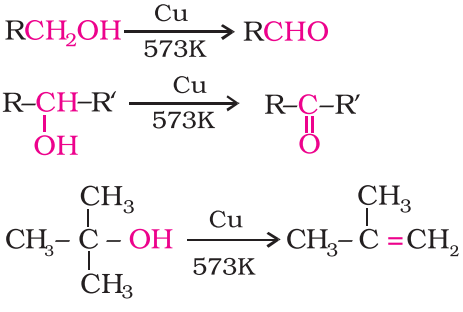
$$CH_3 - CH = CH - CH_2OH \xrightarrow{PCC} CH_3 - CH = CH - CHO$$

Secondary alcohols are oxidised to ketones by chromic anhyride (CrO_3).



Tertiary alcohols do not undergo oxidation reaction. Under strong reaction conditions such as strong oxidising agents ($KMnO_4$) and elevated temperatures, cleavage of various C-C bonds takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.

When the vapours of a primary or a secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place and an aldehyde or a ketone is formed while tertiary alcohols undergo dehydration.



Biological oxidation of methanol and ethanol in the body produces the corresponding aldehyde followed by the acid. At times the alcoholics, by mistake, drink ethanol, mixed with methanol also called denatured alcohol. In the body, methanol is oxidised first to methanal and then to methanoic acid, which may cause blindness and death. A methanol poisoned patient is treated by giving intravenous infusions of diluted ethanol. The enzyme responsible for oxidation of aldehyde (HCHO) to acid is swamped allowing time for kidneys to excrete methanol.

(c) Reactions of phenols

Following reactions are shown by phenols only.

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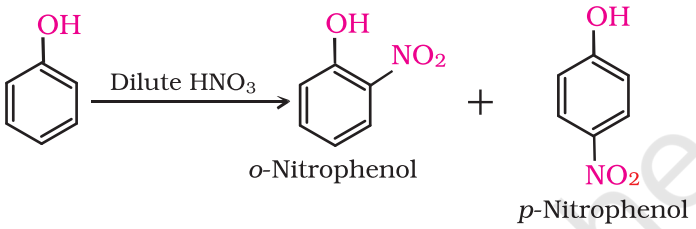
1. *Electrophilic aromatic substitution*

In phenols, the reactions that take place on the aromatic ring are electrophilic substitution reactions (Unit 9, Class XI). The –OH group attached to the benzene ring activates it towards electrophilic substitution. Also, it directs the incoming group to *ortho* and *para* positions in the ring as these positions become electron rich due to the resonance effect caused by –OH group. The resonance structures are shown under acidity of phenols.

Common electrophilic aromatic substitution reactions taking place in phenol are as follows:

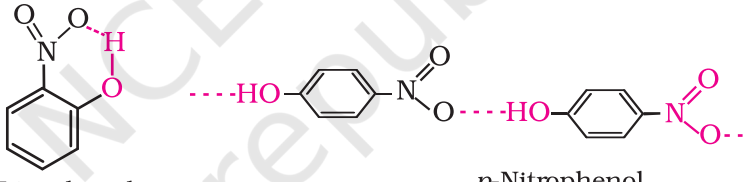
(i) Nitration: With dilute nitric acid at low temperature (298 K), phenol yields a mixture of *ortho* and *para* nitrophenols.



o-Nitrophenol

p-Nitrophenol

The *ortho* and *para* isomers can be separated by steam distillation. *o*-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.

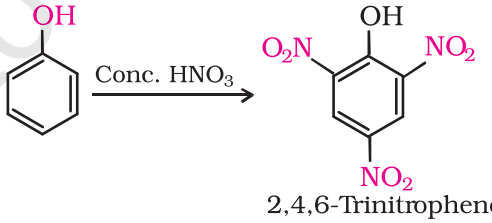


o-Nitrophenol (Intramolecular H-bonding)

p-Nitrophenol (Intermolecular H-bonding)

2, 4, 6 - Trinitrophenol is a strong acid due to the presence of three electron withdrawing –NO_2 groups which facilitate the release of hydrogen ion.

With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol. The product is commonly known as picric acid. The yield of the reaction product is poor.



2,4,6-Trinitrophenol (Picric acid)

Nowadays picric acid is prepared by treating phenol first with concentrated sulphuric acid which converts it to phenol-2,4-disulphonic acid, and then with concentrated nitric acid to get 2,4,6-trinitrophenol. Can you write the equations of the reactions involved?

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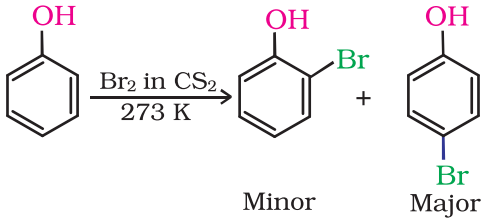
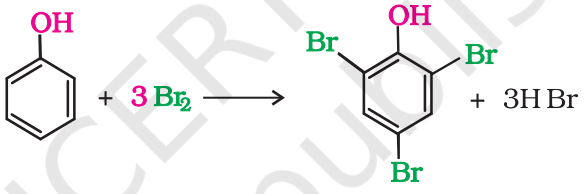
(ii) *Halogenation:* On treating phenol with bromine, different reaction products are formed under different experimental conditions.

(a) When the reaction is carried out in solvents of low polarity such as $CHCl_3$ or CS_2 and at low temperature, monobromophenols are formed.



The usual halogenation of benzene takes place in the presence of a Lewis acid, such as $FeBr_3$ (Unit 6, Class XII), which polarises the halogen molecule. In case of phenol, the polarisation of bromine molecule takes place even in the absence of Lewis acid. It is due to the highly activating effect of –OH group attached to the benzene ring.

(b) When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.



2,4,6-Tribromophenol

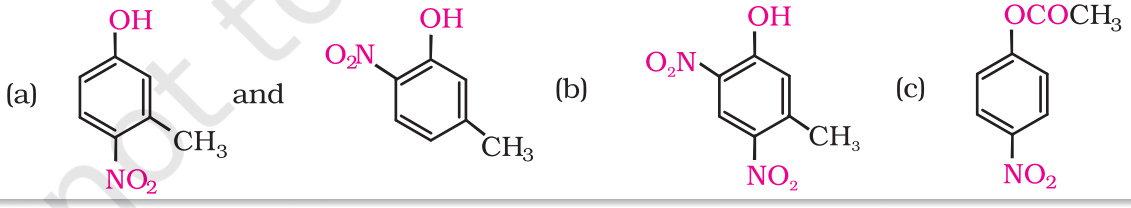
Example 7.5 Write the structures of the major products expected from the following reactions:

(a) Mononitration of 3-methylphenol

(b) Dinitration of 3-methylphenol

(c) Mononitration of phenyl methanoate.

Solution The combined influence of –OH and $–CH_3$ groups determine the position of the incoming group.



2. Kolbe's reaction

Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. *Ortho* hydroxybenzoic acid is formed as the main reaction product.

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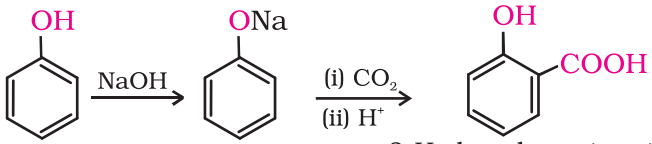
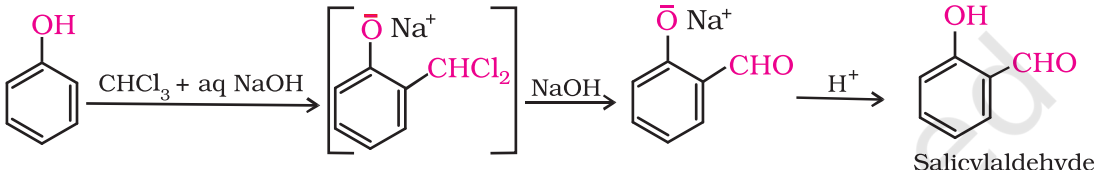


2-Hydroxybenzoic acid
(Salicylic acid)

3. *Reimer-Tiemann reaction*

On treating phenol with chloroform in the presence of sodium hydroxide, a –CHO group is introduced at *ortho* position of benzene ring. This reaction is known as *Reimer - Tiemann reaction*.

The intermediate substituted benzal chloride is hydrolysed in the presence of alkali to produce salicylaldehyde.

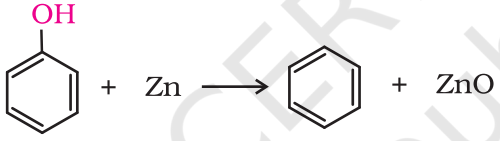


Intermediate

Salicylaldehyde

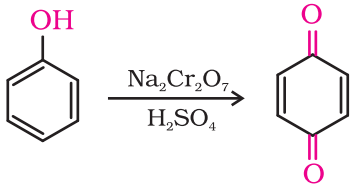
4. *Reaction of phenol with zinc dust*

Phenol is converted to benzene on heating with zinc dust.



5. *Oxidation*

Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone. In the presence of air, phenols are slowly oxidised to dark coloured mixtures containing quinones.



benzoquinone

Intext Questions

7.6 Give structures of the products you would expect when each of the following alcohol reacts with (a) HCl –$ZnCl_2$ (b) HBr and (c) $SOCl_2$.
(i) Butan-1-ol (ii) 2-Methylbutan-2-ol

7.7 Predict the major product of acid catalysed dehydration of
(i) 1-methylcyclohexanol and (ii) butan-1-ol

7.8 *Ortho* and *para* nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.

7.9 Write the equations involved in the following reactions:
(i) Reimer - Tiemann reaction (ii) Kolbe's reaction

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7.5 Some Commercially Important Alcohols

Methanol and ethanol are among the two commercially important alcohols.

1. Methanol

Methanol, CH_3OH, also known as 'wood spirit', was produced by destructive distillation of wood. Today, most of the methanol is produced by catalytic hydrogenation of carbon monoxide at high pressure and temperature and in the presence of ZnO – Cr_2O_3 catalyst.

$$CO + 2H_2 \xrightarrow[200\text{-}300 \text{ atm}, 573\text{-}673 \text{ K}]{ZnO\text{-}Cr_2O_3} CH_3OH$$

Methanol is a colourless liquid and boils at 337 K. It is highly poisonous in nature. Ingestion of even small quantities of methanol can cause blindness and large quantities causes even death. Methanol is used as a solvent in paints, varnishes and chiefly for making formaldehyde.

2. Ethanol

Ethanol, C_2H_5OH, is obtained commercially by fermentation, the oldest method is from sugars. The sugar in molasses, sugarcane or fruits such as grapes is converted to glucose and fructose, (both of which have the formula $C_6H_{12}O_6$), in the presence of an enzyme, invertase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which is found in yeast.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Ingestion of ethanol acts on the central nervous system. In moderate amounts, it affects judgment and lowers inhibitions. Higher concentrations cause nausea and loss of consciousness. Even at higher concentrations, it interferes with spontaneous respiration and can be fatal.

In wine making, grapes are the source of sugars and yeast. As grapes ripen, the quantity of sugar increases and yeast grows on the outer skin. When grapes are crushed, sugar and the enzyme come in contact and fermentation starts. Fermentation takes place in anaerobic conditions i.e. in absence of air. Carbon dioxide is released during fermentation.

The action of zymase is inhibited once the percentage of alcohol formed exceeds 14 percent. If air gets into fermentation mixture, the oxygen of air oxidises ethanol to ethanoic acid which in turn destroys the taste of alcoholic drinks.

Ethanol is a colourless liquid with boiling point 351 K. It is used as a solvent in paint industry and in the preparation of a number of carbon compounds. The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). It is known as **denaturation** of alcohol.

Nowadays, large quantities of ethanol are obtained by hydration of ethene (Section 7.4).

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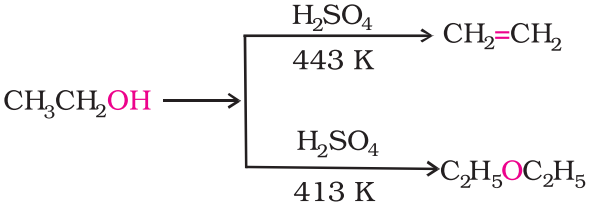
7.6.1 Preparation of Ethers

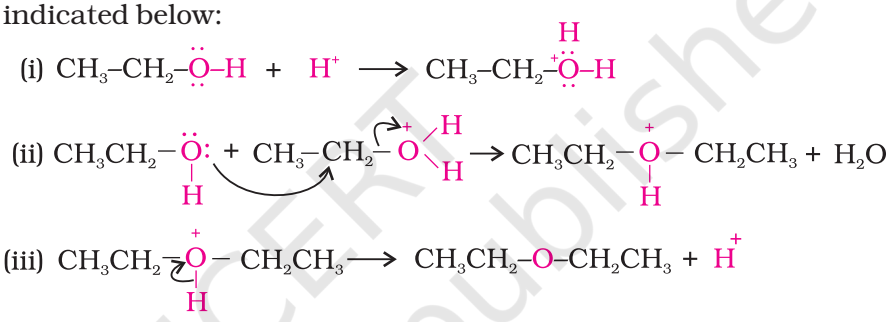
1. By dehydration of alcohols

Alcohols undergo dehydration in the presence of protic acids (H_2SO_4, H_3PO_4). The formation of the reaction product, alkene or ether depends on the reaction conditions. For example, ethanol is dehydrated to ethene in the presence of sulphuric acid at 443 K. At 413 K, ethoxyethane is the main product.

Diethyl ether has been used widely as an inhalation anaesthetic. But due to its slow effect and an unpleasant recovery period, it has been replaced, as an anaesthetic, by other compounds.



The formation of ether is a nucleophilic bimolecular reaction (S_N2) involving the attack of alcohol molecule on a protonated alcohol, as indicated below:



Acidic dehydration of alcohols, to give an alkene is also associated with substitution reaction to give an ether.

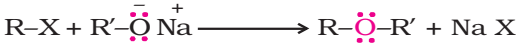
The method is suitable for the preparation of ethers having primary alkyl groups only. The alkyl group should be unhindered and the temperature be kept low. Otherwise the reaction favours the formation of alkene. The reaction follows S_N1 pathway when the alcohol is secondary or tertiary about which you will learn in higher classes. However, the dehydration of secondary and tertiary alcohols to give corresponding ethers is unsuccessful as elimination competes over substitution and as a consequence, alkenes are easily formed.

Can you explain why is bimolecular dehydration not appropriate for the preparation of ethyl methyl ether?

2. Williamson synthesis

Alexander William Williamson (1824–1904) was born in London of Scottish parents. In 1849, he became Professor of Chemistry at University College, London.

It is an important laboratory method for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide.



Ethers containing substituted alkyl groups (secondary or tertiary) may also be prepared by this method. The reaction involves S_N2 attack of an alkoxide ion on primary alkyl halide.

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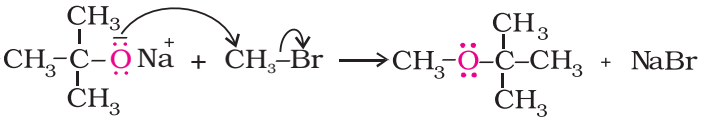
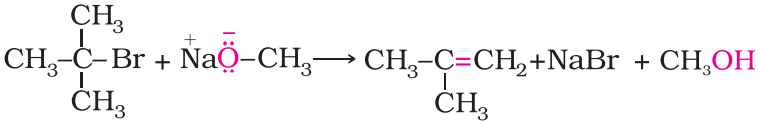


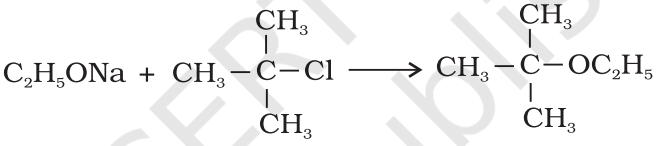
Better results are obtained if the alkyl halide is primary. In case of secondary and tertiary alkyl halides, elimination competes over substitution. If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed. For example, the reaction of CH_3ONa with $(CH_3)_3C–Br$ gives exclusively 2-methylpropene.



2-Methylpropene

It is because alkoxides are not only nucleophiles but strong bases as well. They react with alkyl halides leading to elimination reactions.

Example 7.6 The following is not an appropriate reaction for the preparation of t-butyl ethyl ether.

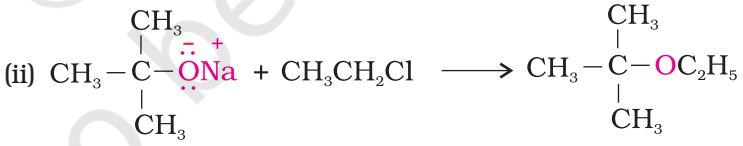


(i) What would be the major product of this reaction ?

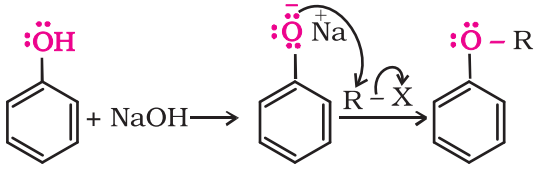
(ii) Write a suitable reaction for the preparation of t-butylethyl ether.

Solution

(i) The major product of the given reaction is 2-methylprop-1-ene. It is because sodium ethoxide is a strong nucleophile as well as a strong base. Thus elimination reaction predominates over substitution.

(ii) 

Phenols are also converted to ethers by this method. In this, phenol is used as the phenoxide moiety.



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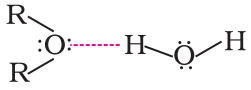
7.6.2 Physical Properties

The C-O bonds in ethers are polar and thus, ethers have a net dipole moment. The weak polarity of ethers do not appreciably affect their boiling points which are comparable to those of the alkanes of comparable molecular masses but are much lower than the boiling points of alcohols as shown in the following cases:

Formula	$CH_3(CH_2)_3CH_3$ n-Pentane	C_2H_5-O-C_2H_5 Ethoxyethane	$CH_3(CH_2)_3$-OH Butan-1-ol
b.p./K	309.1	307.6	390

The large difference in boiling points of alcohols and ethers is due to the presence of hydrogen bonding in alcohols.

The miscibility of ethers with water resembles those of alcohols of the same molecular mass. Both ethoxyethane and butan-1-ol are miscible to almost the same extent i.e., 7.5 and 9 g per 100 mL water, respectively while pentane is essentially immiscible with water. Can you explain this observation ? This is due to the fact that just like alcohols, oxygen of ether can also form hydrogen bonds with water molecule as shown:



7.6.3 Chemical Reactions

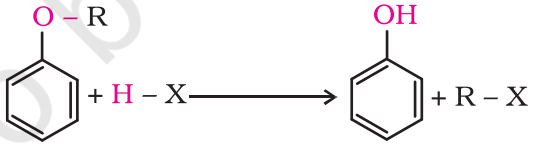
1. Cleavage of C–O bond in ethers

Ethers are the least reactive of the functional groups. The cleavage of C-O bond in ethers takes place under drastic conditions with excess of hydrogen halides. The reaction of dialkyl ether gives two alkyl halide molecules.

$$R–O–R + HX \longrightarrow RX + R–OH$$

$$R–OH + HX \longrightarrow R–X + H_2O$$

Alkyl aryl ethers are cleaved at the alkyl-oxygen bond due to the more stable aryl-oxygen bond. The reaction yields phenol and alkyl halide.



Ethers with two different alkyl groups are also cleaved in the same manner.

$$R–O–R' + HX \longrightarrow R–X + R'–OH$$

The order of reactivity of hydrogen halides is as follows: HI > HBr > HCl. The cleavage of ethers takes place with concentrated HI or HBr at high temperature.

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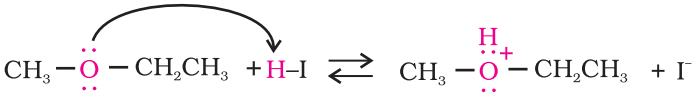
Mechanism

The reaction of an ether with concentrated HI starts with protonation of ether molecule.

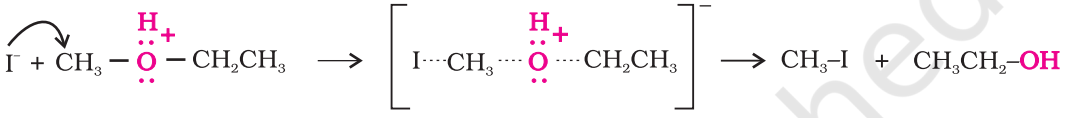
Step 1:



The reaction takes place with HBr or HI because these reagents are sufficiently acidic.

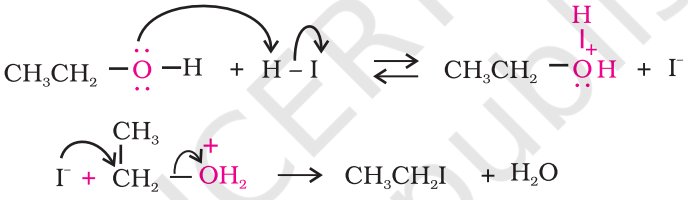
Step 2:

Iodide is a good nucleophile. It attacks the least substituted carbon of the oxonium ion formed in step 1 and displaces an alcohol molecule by S_N2 mechanism. Thus, in the cleavage of mixed ethers with two different alkyl groups, the alcohol and alkyl iodide formed, depend on the nature of alkyl groups. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide (S_N2 reaction).

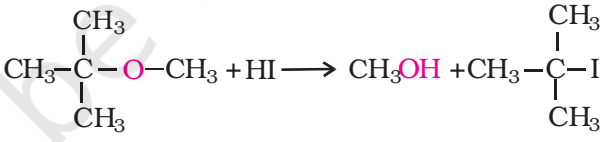


When HI is in excess and the reaction is carried out at high temperature, ethanol reacts with another molecule of HI and is converted to ethyl iodide.

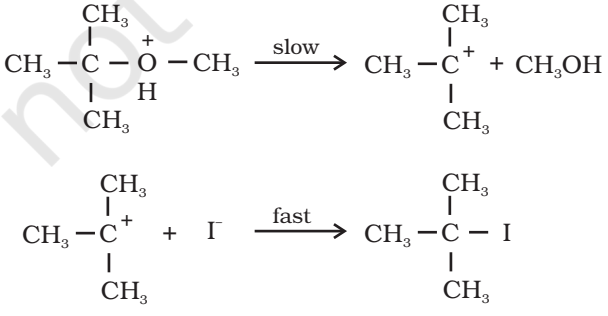
Step 3:

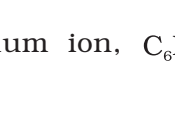


However, when one of the alkyl group is a tertiary group, the halide formed is a tertiary halide.



It is because in step 2 of the reaction, the departure of leaving group ($HO–CH_3$) creates a more stable carbocation [$(CH_3)_3C^+$], and the reaction follows S_N1 mechanism.



In case of anisole, methylphenyl oxonium ion,  is formed by protonation of ether. The bond between $O–CH_3$ is weaker than the bond between $O–C_6H_5$ because the carbon of phenyl group is sp^2 hybridised and there is a partial double bond character.

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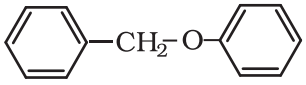
Therefore the attack by I^- ion breaks O–CH_3 bond to form CH_3I. Phenols do not react further to give halides because the sp^2 hybridised carbon of phenol cannot undergo nucleophilic substitution reaction needed for conversion to the halide.

Example 7.7

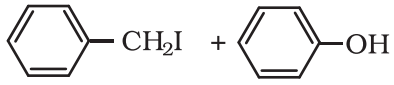
Give the major products that are formed by heating each of the following ethers with HI.

(i) $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-O-CH_2-CH_3$ (ii) $CH_3-CH_2-CH_2-O-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2CH_3$

(iii) 

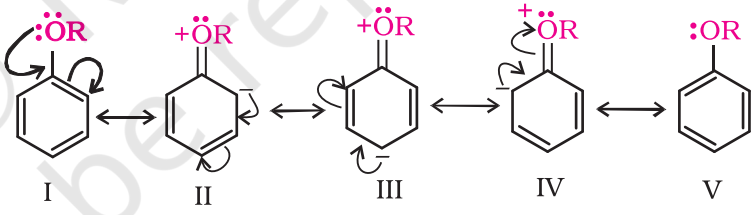
Solution

(i) $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH + CH_3CH_2I$ (ii) $CH_3CH_2CH_2OH + CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-I$

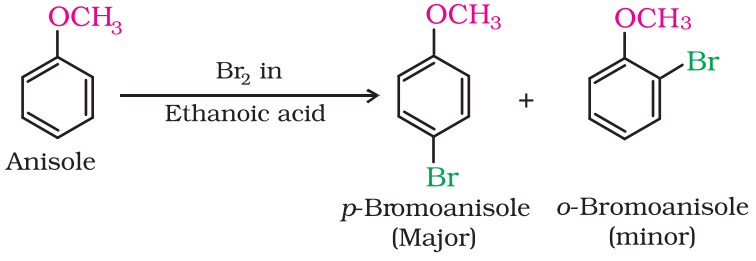
(iii) 

2. *Electrophilic substitution*

The alkoxy group (-OR) is *ortho*, *para* directing and activates the aromatic ring towards electrophilic substitution in the same way as in phenol.



(i) *Halogenation*: Phenylalkyl ethers undergo usual halogenation in the benzene ring, *e.g.*, anisole undergoes bromination with bromine in ethanoic acid even in the absence of iron (III) bromide catalyst. It is due to the activation of benzene ring by the methoxy group. *Para* isomer is obtained in 90% yield.



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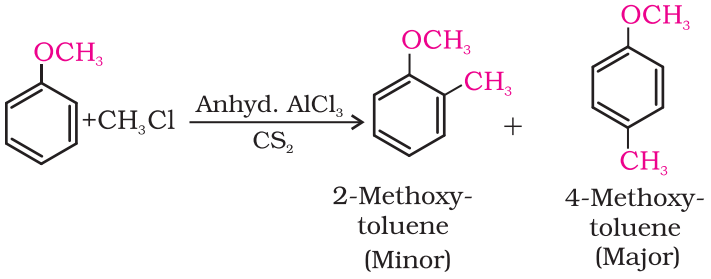
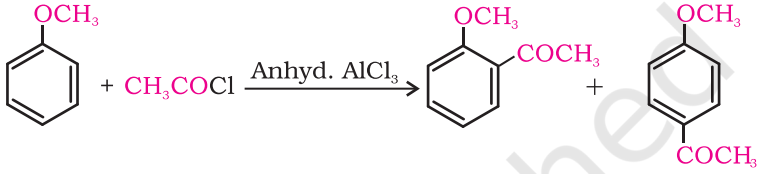
(ii) *Friedel-Crafts reaction*: Anisole undergoes Friedel-Crafts reaction, *i.e.*, the alkyl and acyl groups are introduced at *ortho* and *para* positions by reaction with alkyl halide and acyl halide in the presence of anhydrous aluminium chloride (a Lewis acid) as catalyst.

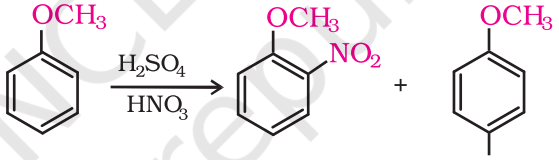


2-Methoxy-toluene (Minor) + 4-Methoxy-toluene (Major)



Ethanoyl chloride; 2-Methoxy-acetophenone (Minor); 4-Methoxy-acetophenone (Major)

(iii) *Nitration*: Anisole reacts with a mixture of concentrated sulphuric and nitric acids to yield a mixture of *ortho* and *para* nitroanisole.

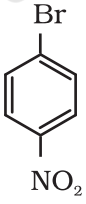


2-Nitroanisole (Minor); 4-Nitroanisole (Major)

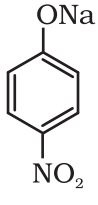
Intext Questions

7.10 Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol.

7.11 Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?

(i) 

+ CH_3ONa

(ii) 

+ CH_3Br

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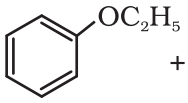
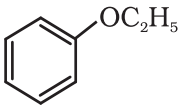
7.12 Predict the products of the following reactions:

(i) $CH_3 - CH_2 - CH_2 - O - CH_3 + HBr \rightarrow$

(ii)  + HBr ⟶

(iii)  $\xrightarrow[\text{Conc. } HNO_3]{\text{Conc. } H_2SO_4}$

(iv) $(CH_3)_3 C - OC_2H_5 \xrightarrow{HI}$

Summary

Alcohols and **phenols** are classified (i) on the basis of the number of hydroxyl groups and (ii) according to the hybridisation of the carbon atom, sp^3 or sp^2 to which the –OH group is attached. **Ethers** are classified on the basis of groups attached to the oxygen atom.

Alcohols may be prepared (1) by hydration of alkenes (i) in presence of an acid and (ii) by hydroboration-oxidation reaction (2) from carbonyl compounds by (i) catalytic reduction and (ii) the action of Grignard reagents. Phenols may be prepared by (1) substitution of (i) halogen atom in haloarenes and (ii) sulphonic acid group in aryl sulphonic acids, by –OH group (2) by hydrolysis of diazonium salts and (3) industrially from cumene.

Alcohols are higher boiling than other classes of compounds, namely hydrocarbons, ethers and haloalkanes of comparable molecular masses. The ability of alcohols, phenols and ethers to form intermolecular hydrogen bonding with water makes them soluble in it.

Alcohols and phenols are acidic in nature. **Electron withdrawing groups** in phenol increase its acidic strength and **electron releasing groups** decrease it.

Alcohols undergo nucleophilic substitution with hydrogen halides to yield alkyl halides. Dehydration of alcohols gives alkenes. On oxidation, primary alcohols yield aldehydes with mild oxidising agents and carboxylic acids with strong oxidising agents while secondary alcohols yield ketones. Tertiary alcohols are resistant to oxidation.

The presence of –OH group in phenols activates the aromatic ring towards **electrophilic substitution** and directs the incoming group to *ortho* and *para* positions due to resonance effect. **Reimer-Tiemann reaction** of phenol yields salicylaldehyde. In presence of sodium hydroxide, phenol generates phenoxide ion which is even more reactive than phenol. Thus, in alkaline medium, phenol undergoes **Kolbe's reaction**.

Ethers may be prepared by (i) dehydration of alcohols and (ii) **Williamson synthesis**. The boiling points of ethers resemble those of alkanes while their solubility is comparable to those of alcohols having same molecular mass. The C–O bond in ethers can be cleaved by hydrogen halides. In electrophilic substitution, the alkoxy group activates the aromatic ring and directs the incoming group to ortho and para positions.

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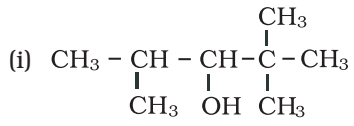
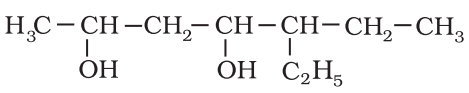
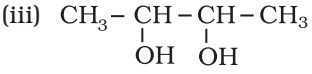
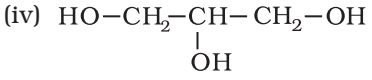
Exercises

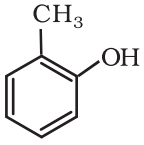
7.1 Write IUPAC names of the following compounds:

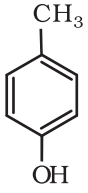
(i) 

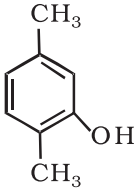
(ii) 

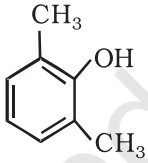
(iii) 

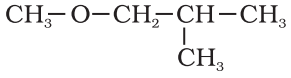
(iv) 

(v) 

(vi) 

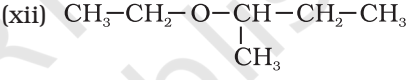
(vii) 

(viii) 

(ix) 

(x) $C_6H_5–O–C_2H_5$

(xi) $C_6H_5–O–C_7H_{15}$(n–)

(xii) 

7.2 Write structures of the compounds whose IUPAC names are as follows:

(i) 2-Methylbutan-2-ol
(ii) 1-Phenylpropan-2-ol
(iii) 3,5-Dimethylhexane –1, 3, 5-triol
(iv) 2,3 – Diethylphenol
(v) 1 – Ethoxypropane
(vi) 2-Ethoxy-3-methylpentane
(vii) Cyclohexylmethanol
(viii) 3-Cyclohexylpentan-3-ol
(ix) Cyclopent-3-en-1-ol
(x) 4-Chloro-3-ethylbutan-1-ol.

7.3 (i) Draw the structures of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC names.

(ii) Classify the isomers of alcohols in question 11.3 (i) as primary, secondary and tertiary alcohols.

7.4 Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

7.5 Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

7.6 What is meant by hydroboration-oxidation reaction? Illustrate it with an example.

7.7 Give the structures and IUPAC names of monohydric phenols of molecular formula, C_7H_8O.

7.8 While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

7.9 Give the equations of reactions for the preparation of phenol from cumene.

7.10 Write chemical reaction for the preparation of phenol from chlorobenzene.

7.11 Write the mechanism of hydration of ethene to yield ethanol.

7.12 You are given benzene, conc. H_2SO_4 and NaOH. Write the equations for the preparation of phenol using these reagents.

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7.13 Show how will you synthesise:

(i) 1-phenylethanol from a suitable alkene.

(ii) cyclohexylmethanol using an alkyl halide by an S_N2 reaction.

(iii) pentan-1-ol using a suitable alkyl halide?

7.14 Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

7.15 Explain why is *ortho* nitrophenol more acidic than *ortho* methoxyphenol ?

7.16 Explain how does the –OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?

7.17 Give equations of the following reactions:

(i) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.

(ii) Bromine in CS_2 with phenol.

(iii) Dilute HNO_3 with phenol.

(iv) Treating phenol wih chloroform in presence of aqueous NaOH.

7.18 Explain the following with an example.

(i) Kolbe's reaction.

(ii) Reimer-Tiemann reaction.

(iii) Williamson ether synthesis.

(iv) Unsymmetrical ether.

7.19 Write the mechanism of acid dehydration of ethanol to yield ethene.

7.20 How are the following conversions carried out?

(i) Propene → Propan-2-ol.

(ii) Benzyl chloride → Benzyl alcohol.

(iii) Ethyl magnesium chloride → Propan-1-ol.

(iv) Methyl magnesium bromide → 2-Methylpropan-2-ol.

7.21 Name the reagents used in the following reactions:

(i) Oxidation of a primary alcohol to carboxylic acid.

(ii) Oxidation of a primary alcohol to aldehyde.

(iii) Bromination of phenol to 2,4,6-tribromophenol.

(iv) Benzyl alcohol to benzoic acid.

(v) Dehydration of propan-2-ol to propene.

(vi) Butan-2-one to butan-2-ol.

7.22 Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

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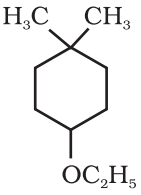
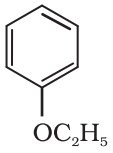
7.23 Give IUPAC names of the following ethers:

(i) $C_2H_5OCH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH_3$ (ii) $CH_3OCH_2CH_2Cl$ (iii) $O_2N-C_6H_4-OCH_3(p)$

(iv) $CH_3CH_2CH_2OCH_3$ (v)  (vi) 

7.24 Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

(i) 1-Propoxypropane (ii) Ethoxybenzene

(iii) 2-Methoxy-2-methylpropane (iv) 1-Methoxyethane

7.25 Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.

7.26 How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.

7.27 Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

7.28 Write the equation of the reaction of hydrogen iodide with:
(i) 1-propoxypropane (ii) methoxybenzene and (iii) benzyl ethyl ether.

7.29 Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituents to ortho and para positions in benzene ring.

7.30 Write the mechanism of the reaction of HI with methoxymethane.

7.31 Write equations of the following reactions:

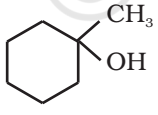
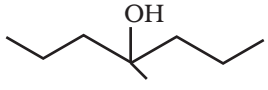
(i) Friedel-Crafts reaction – alkylation of anisole.

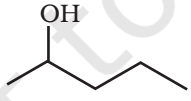
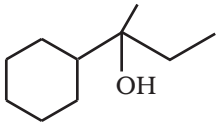
(ii) Nitration of anisole.

(iii) Bromination of anisole in ethanoic acid medium.

(iv) Friedel-Craft's acetylation of anisole.

7.32 Show how would you synthesise the following alcohols from appropriate alkenes?

(i)  (ii) 

(iii)  (iv) 

7.33 When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-\underset{\displaystyle OH}{\overset{\displaystyle |}{CH}}-CH_3 \xrightarrow{HBr} CH_3-\overset{\displaystyle Br}{\overset{\displaystyle |}{\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}}}-CH_2-CH_3$$

Give a mechanism for this reaction.

(Hint : The secondary carbocation formed in step II rearranges to a more stable tertiary carbocation by a hydride ion shift from 3rd carbon atom.

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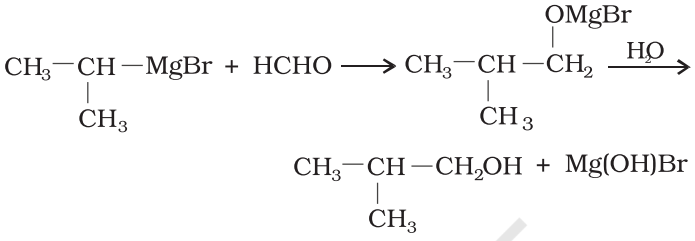
Answers to Some Intext Questions

7.1 Primary alcohols — (i), (ii), (iii)
Secondary alcohols — (iv) and (v)
Tertiary alcohols — (vi)

7.2 Allylic alcohols — (ii) and (vi)

7.3 (i) 4-Chloro-3-ethyl-2-(1-methylethyl)-butan-1-ol
(ii) 2, 5-Dimethylhexane-1,3-diol
(iii) 3-Bromocyclohexanol
(iv) Hex-1-en-3-ol
(v) 2-Bromo-3-methylbut-2-en-1-ol

7.4 (i)



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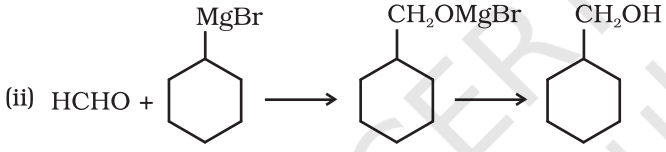
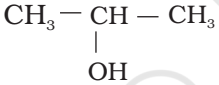


7.5 (i)



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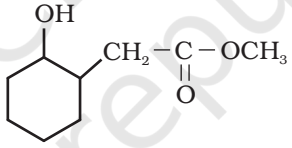

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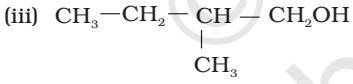
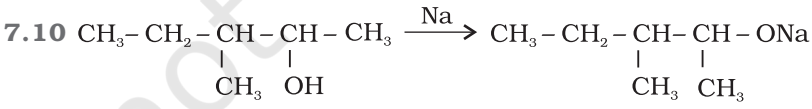
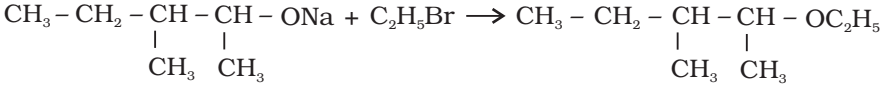


7.7 (i) 1-Methylcyclohexene

(ii) A Mixture of but-1-ene and but-2-ene. But-2-ene is the major product formed due to rearrangement to give secondary carbocation.

7.10





2-Ethoxy-3-methylpentane

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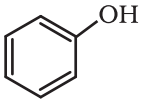
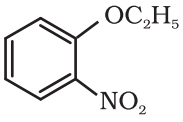
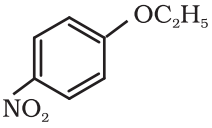
7.11 (ii)

7.12 (i) $CH_3CH_2CH_2OH + CH_3Br$

(ii)  + C_2H_5Br

(iii)  + 

(iv) $(CH_3)_3C - I + C_2H_5OH$

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Unit

8

Aldehydes, Ketones and Carboxylic Acids

Objectives

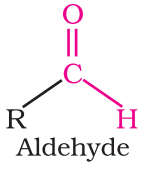
After studying this Unit, you will be able to

- write the common and IUPAC names of aldehydes, ketones and carboxylic acids;
- write the structures of the compounds containing functional groups namely carbonyl and carboxyl groups;
- describe the important methods of preparation and reactions of these classes of compounds;
- correlate physical properties and chemical reactions of aldehydes, ketones and carboxylic acids, with their structures;
- explain the mechanism of a few selected reactions of aldehydes and ketones;
- understand various factors affecting the acidity of carboxylic acids and their reactions;
- describe the uses of aldehydes, ketones and carboxylic acids.

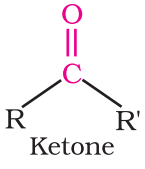
Carbonyl compounds are of utmost importance to organic chemistry. They are constituents of fabrics, flavourings, plastics and drugs.

In the previous Unit, you have studied organic compounds with functional groups containing carbon-oxygen single bond. In this Unit, we will study about the organic compounds containing carbon-oxygen double bond (>C=O) called carbonyl group, which is one of the most important functional groups in organic chemistry.

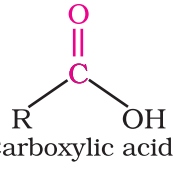
In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in the ketones, it is bonded to two carbon atoms. The carbonyl compounds in which carbon of carbonyl group is bonded to carbon or hydrogen and oxygen of hydroxyl moiety (-OH) are known as carboxylic acids, while in compounds where carbon is attached to carbon or hydrogen and nitrogen of -NH_2 moiety or to halogens are called amides and acyl halides respectively. Esters and anhydrides are derivatives of carboxylic acids. The general formulas of these classes of compounds are given below:



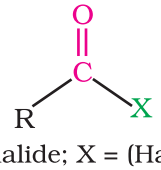
Aldehyde



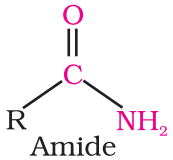
Ketone



Carboxylic acid



Acyl halide; X = (Halogen)



Amide

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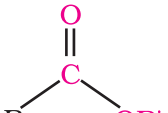
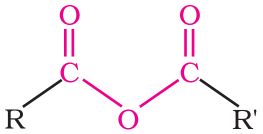
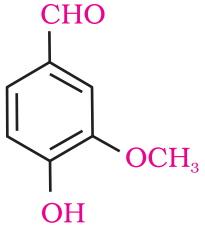
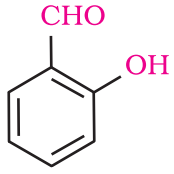
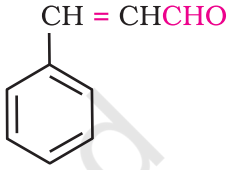

Ester


Acid anhydride

Aldehydes, ketones and carboxylic acids are widespread in plants and animal kingdom. They play an important role in biochemical processes of life. They add fragrance and flavour to nature, for example, vanillin (from vanilla beans), salicylaldehyde (from meadow sweet) and cinnamaldehyde (from cinnamon) have very pleasant fragrances.


Vanillin


Salicylaldehyde


Cinnamaldehyde

They are used in many food products and pharmaceuticals to add flavours. Some of these families are manufactured for use as solvents (i.e., acetone) and for preparing materials like adhesives, paints, resins, perfumes, plastics, fabrics, etc.

8.1 Nomenclature and Structure of Carbonyl Group

8.1.1 Nomenclature

I. *Aldehydes and ketones*

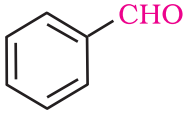
Aldehydes and ketones are the simplest and most important carbonyl compounds.

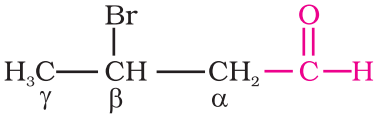
There are two systems of nomenclature of aldehydes and ketones.

(a) Common names

Aldehydes and ketones are often called by their common names instead of IUPAC names. The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids [Section 8.6.1] by replacing the ending *–ic* of acid with aldehyde. At the same time, the names reflect the Latin or Greek term for the original source of the acid or aldehyde. The location of the substituent in the carbon chain is indicated by Greek letters α, β, γ, δ, etc. The α-carbon being the one directly linked to the aldehyde group, β-carbon the next, and so on. For example

Acetaldehyde


Benzaldehyde


β-Bromobutyraldehyde

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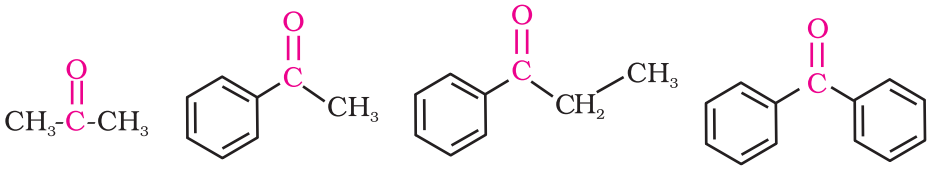
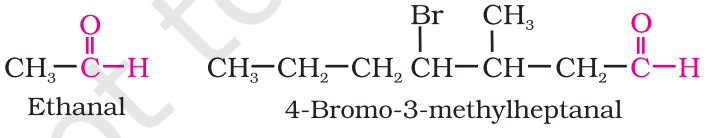
The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group. The locations of substituents are indicated by Greek letters, α α′, β β′ and so on beginning with the carbon atoms next to the carbonyl group, indicated as αα′. Some ketones have historical common names, the simplest dimethyl ketone is called acetone. Alkyl phenyl ketones are usually named by adding the name of acyl group as prefix to the word phenone. For example



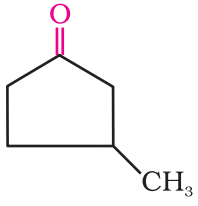
Acetone Acetophenone Propiophenone Benzophenone

(b) *IUPAC names*

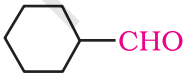
The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending *–e* with *–al* and *–one* respectively. In case of aldehydes the longest carbon chain is numbered starting from the carbon of the aldehyde group while in case of ketones the numbering begins from the end nearer to the carbonyl group. The substituents are prefixed in alphabetical order along with numerals indicating their positions in the carbon chain. The same applies to cyclic ketones, where the carbonyl carbon is numbered one. When the aldehyde group is attached to a ring, the suffix carbaldehyde is added after the full name of the cycloalkane. The numbering of the ring carbon atoms start from the carbon atom attached to the aldehyde group. The name of the simplest aromatic aldehyde carrying the aldehyde group on a benzene ring is benzenecarbaldehyde. However, the common name benzaldehyde is also accepted by IUPAC. Other aromatic aldehydes are hence named as substituted benzaldehydes.



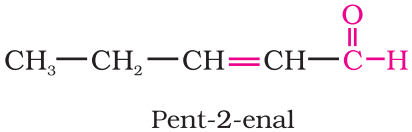
Ethanal 4-Bromo-3-methylheptanal



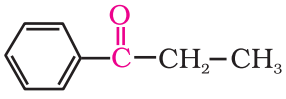
3-Methylcyclopentanone



Cyclohexanecarbaldehyde



Pent-2-enal



1-Phenylpropan-1-one

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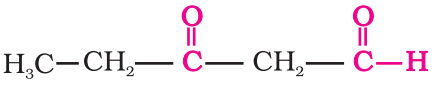
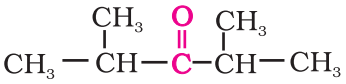
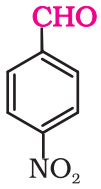


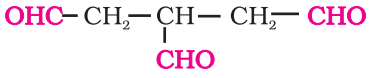
3-Oxopentanal



2,4-Dimethylpentan-3-one



4-Nitrobenzenecarbaldehyde
or
4-Nitrobenzaldehyde

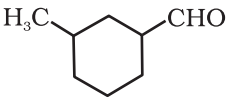
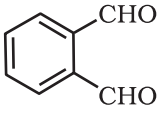
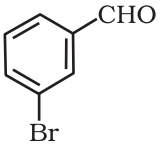
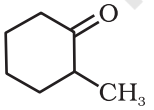


Propane–1,2,3-tricarbaldehyde

Note: To give identical treatment to all aldehydic groups, the compound is named as shown above.

The common and IUPAC names of some aldehydes and ketones are given in Table 8.1.

Table 8.1: Common and IUPAC Names of Some Aldehydes and Ketones

Structure	Common name	IUPAC name
Aldehydes		
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
$(CH_3)_2CHCHO$	Isobutyraldehyde	2-Methylpropanal
	γ-Methylcyclohexanecarbaldehyde	3-Methylcyclohexanecarbaldehyde
$CH_3CH(OCH_3)CHO$	α-Methoxypropionaldehyde	2-Methoxypropanal
$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde	Pentanal
$CH_2=CHCHO$	Acrolein	Prop-2-enal
	Phthaldehyde	Benzene-1,2-dicarbaldehyde
	*m*-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
Ketones		
$CH_3COCH_2CH_2CH_3$	Methyl *n*-propyl ketone	Pentan-2-one
$(CH_3)_2CHCOCH(CH_3)_2$	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α-Methylcyclohexanone	2-Methylcyclohexanone
$(CH_3)_2C=CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one

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8.1.2 Structure of the Carbonyl Group

The carbonyl carbon atom is sp^2-hybridised and forms three sigma (σ) bonds. The fourth valence electron of carbon remains in its *p*-orbital and forms a π-bond with oxygen by overlap with *p*-orbital of an oxygen. In addition, the oxygen atom also has two non bonding electron pairs. Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane and the π-electron cloud is above and below this plane. The bond angles are approximately 120° as expected of a trigonal coplanar structure (Figure 8.1).

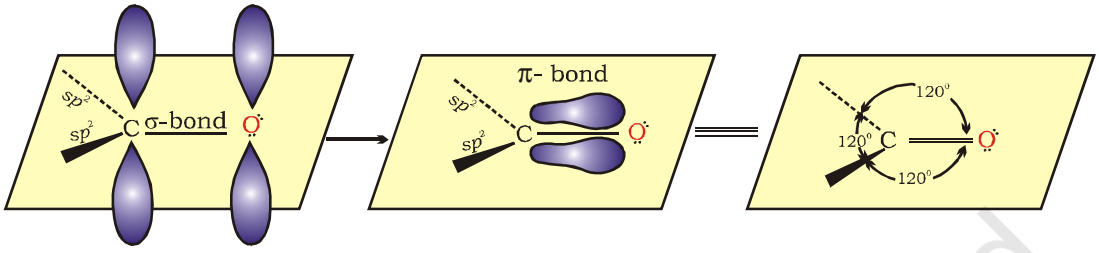
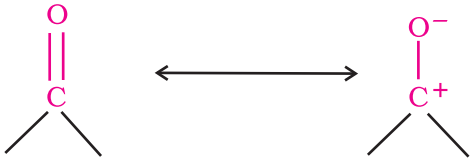


Fig.8.1 Orbital diagram for the formation of carbonyl group

The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen relative to carbon. Hence, the carbonyl carbon is an electrophilic (Lewis acid), and carbonyl oxygen, a nucleophilic (Lewis base) centre. Carbonyl compounds have substantial dipole moments and are polar than ethers. The high polarity of the carbonyl group is explained on the basis of resonance involving a neutral (A) and a dipolar (B) structures as shown.



(A) (B)

Intext Questions

8.1 Write the structures of the following compounds.

(i) α-Methoxypropionaldehyde
(ii) 3-Hydroxybutanal
(iii) 2-Hydroxycyclopentane carbaldehyde
(iv) 4-Oxopentanal
(v) Di-sec. butyl ketone
(vi) 4-Fluoroacetophenone

8.2 Preparation of Aldehydes and Ketones

Some important methods for the preparation of aldehydes and ketones are as follows:

8.2.1 Preparation of Aldehydes and Ketones

1. By oxidation of alcohols

Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively (Unit 7, Class XII).

2. By dehydrogenation of alcohols

This method is suitable for volatile alcohols and is of industrial application. In this method alcohol vapours are passed over heavy metal catalysts (Ag or Cu). Primary and secondary alcohols give aldehydes and ketones, respectively (Unit 7, Class XII).

3. From hydrocarbons

(i) *By ozonolysis of alkenes:* As we know, ozonolysis of alkenes followed by reaction with zinc dust and water gives aldehydes,

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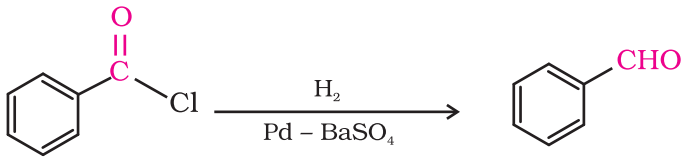
ketones or a mixture of both depending on the substitution pattern of the alkene (Unit 9, Class XI).

(*ii*) *By hydration of alkynes:* Addition of water to ethyne in the presence of H_2SO_4 and $HgSO_4$ gives acetaldehyde. All other alkynes give ketones in this reaction (Unit 9, Class XI).

8.2.2 Preparation of Aldehydes

1. From acyl chloride (acid chloride)

Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate. This reaction is called **Rosenmund reduction**.



Benzoyl chloride Benzaldehyde

2. From nitriles and esters

Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde.

$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3O^+} RCHO$$

This reaction is called **Stephen** reaction.

Alternatively, nitriles are selectively reduced by diisobutylaluminium hydride, (DIBAL-H) to imines followed by hydrolysis to aldehydes:

$$R\text{-}CN \xrightarrow[2.\ H_2O]{1.\ AlH(i\text{-}Bu)_2} R\text{-}CHO$$

$$CH_3 — CH{=}CH\text{-}CH_2CH_2\text{-}CN \xrightarrow[2.\ H_2O]{1.\ AlH(i\text{-}Bu)_2} CH_3 — CH{=}CH\text{-}CH_2CH_2\text{-}CHO$$

Similarly, esters are also reduced to aldehydes with DIBAL-H.

$$CH_3(CH_2)_9 — \overset{O}{\overset{\|}{C}} — OC_2H_5 \xrightarrow[2.\ H_2O]{1.\ DIBAL\text{-}H} CH_3(CH_2)_9 — \overset{O}{\overset{\|}{C}} — H$$

3. From hydrocarbons

Aromatic aldehydes (benzaldehyde and its derivatives) are prepared from aromatic hydrocarbons by the following methods:

(i) By oxidation of methylbenzene

Strong oxidising agents oxidise toluene and its derivatives to benzoic acids. However, it is possible to stop the oxidation at the aldehyde stage with suitable reagents that convert the methyl group to an intermediate that is difficult to oxidise further. The following methods are used for this purpose.

(a) Use of chromyl chloride (CrO_2Cl_2): Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.

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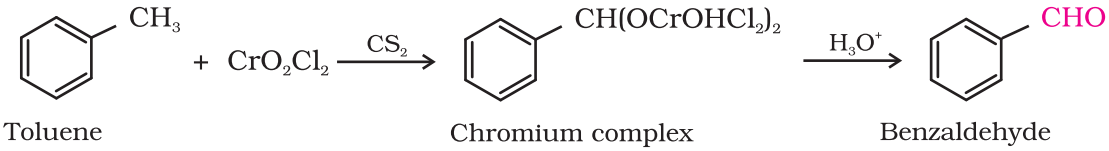
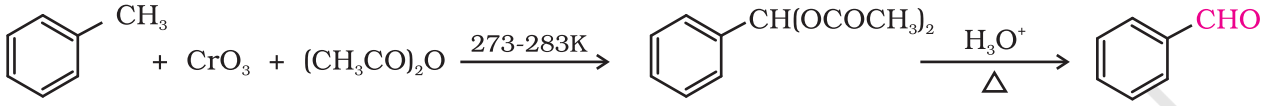


Toluene — Chromium complex — Benzaldehyde

This reaction is called **Etard reaction**.

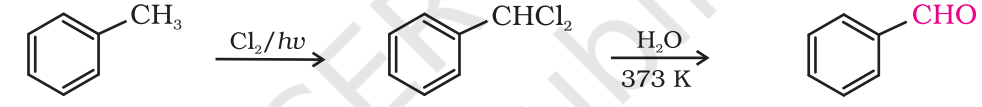
(b) Use of chromic oxide (CrO_3): Toluene or substituted toluene is converted to benzylidene diacetate on treating with chromic oxide in acetic anhydride. The benzylidene diacetate can be hydrolysed to corresponding benzaldehyde with aqueous acid.



Benzaldehyde

(ii) By side chain chlorination followed by hydrolysis

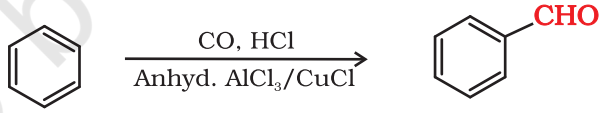
Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde. This is a commercial method of manufacture of benzaldehyde.



Toluene — Benzal chloride — Benzaldehyde

(iii) By Gatterman – Koch reaction

When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.



Benzene — Benzaldehyde

This reaction is known as **Gatterman-Koch** reaction.

8.2.3 Preparation of Ketones

1. From acyl chlorides

Treatment of acyl chlorides with dialkylcadmium, prepared by the reaction of cadmium chloride with Grignard reagent, gives ketones.

$$2\ R-Mg-X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$

$$2\ R'-\underset{\underset{O}{\|}}{C}-Cl + R_2Cd \longrightarrow 2\ R'-\underset{\underset{O}{\|}}{C}-R + CdCl_2$$

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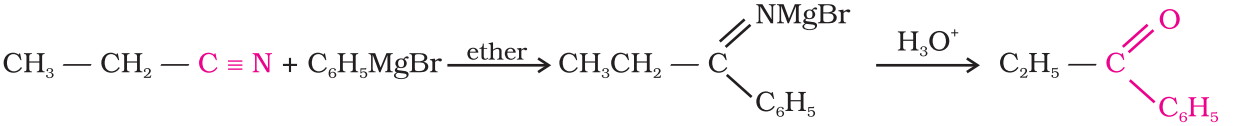
2. *From nitriles*

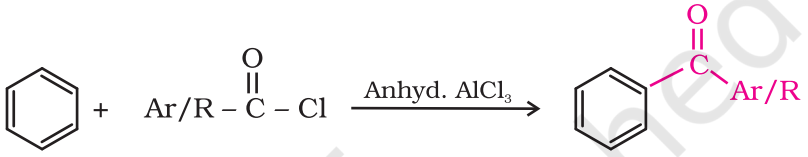
Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.



Propiophenone
(1-Phenylpropanone)

3. *From benzene or substituted benzenes*

When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminium chloride, it affords the corresponding ketone. This reaction is known as **Friedel-Crafts acylation reaction**.



Example 8.1 Give names of the reagents to bring about the following transformations:

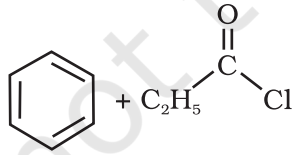
(i) Hexan-1-ol to hexanal
(ii) Cyclohexanol to cyclohexanone
(iii) *p*-Fluorotoluene to *p*-fluorobenzaldehyde
(iv) Ethanenitrile to ethanal
(v) Allyl alcohol to propenal
(vi) But-2-ene to ethanal

Solution

(i) $C_5H_5NH^+CrO_3Cl^-$ (PCC)
(ii) Anhydrous CrO_3
(iii) CrO_3 in the presence of acetic anhydride/ 1. CrO_2Cl_2 2. HOH
(iv) (Diisobutyl)aluminium hydride (DIBAL-H)
(v) PCC
(vi) O_3/H_2O-Zn dust

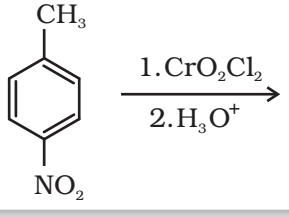
Intext Question

8.2 Write the structures of products of the following reactions;

(i) 

(ii) $(C_6H_5CH_2)_2Cd + 2\ CH_3COCl \rightarrow$

(iii) $H_3C-C\equiv C-H \xrightarrow{Hg^{2+},\ H_2SO_4}$

(iv) 

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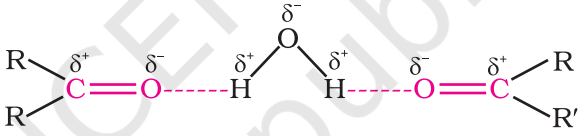
8.3 Physical Properties

The physical properties of aldehydes and ketones are described as follows.

Methanal is a gas at room temperature. Ethanal is a volatile liquid. Other aldehydes and ketones are liquid or solid at room temperature. The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions. Also, their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding. The following compounds of molecular masses 58 and 60 are ranked in order of increasing boiling points.

	b.p.(K)	Molecular Mass
n-Butane	273	58
Methoxyethane	281	60
Propanal	322	58
Acetone	329	58
Propan-1-ol	370	60

The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions, because they form hydrogen bond with water.



However, the solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain. All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform, etc. The lower aldehydes have sharp pungent odours. As the size of the molecule increases, the odour becomes less pungent and more fragrant. In fact, many naturally occurring aldehydes and ketones are used in the blending of perfumes and flavouring agents.

Example 8.2

Arrange the following compounds in the increasing order of their boiling points:

$CH_3CH_2CH_2CHO$, $CH_3CH_2CH_2CH_2OH$, H_5C_2-O-C_2H_5, $CH_3CH_2CH_2CH_3$

Solution

The molecular masses of these compounds are in the range of 72 to 74. Since only butan-1-ol molecules are associated due to extensive intermolecular hydrogen bonding, therefore, the boiling point of butan-1-ol would be the highest. Butanal is more polar than ethoxyethane. Therefore, the intermolecular dipole-dipole attraction is stronger in the former. *n*-Pentane molecules have only weak **van der Waals forces**. Hence increasing order of boiling points of the given compounds is as follows:

$CH_3CH_2CH_2CH_3 < H_5C_2$-O-$C_2H_5 < CH_3CH_2CH_2CHO < CH_3CH_2CH_2CH_2OH$

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Intext Question

8.3 Arrange the following compounds in increasing order of their boiling points.

CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$

8.4 Chemical Reactions

Since aldehydes and ketones both possess the carbonyl functional group, they undergo similar chemical reactions.

1. Nucleophilic addition reactions

Contrary to electrophilic addition reactions observed in alkenes, the aldehydes and ketones undergo nucleophilic addition reactions.

(i) Mechanism of nucleophilic addition reactions

A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp^2 hybridised orbitals of carbonyl carbon (Fig. 8.2). The hybridisation of carbon changes from sp^2 to sp^3 in this process, and a tetrahedral alkoxide intermediate is produced. This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result is addition of Nu^- and H^+ across the carbon oxygen double bond as shown in Fig. 8.2.

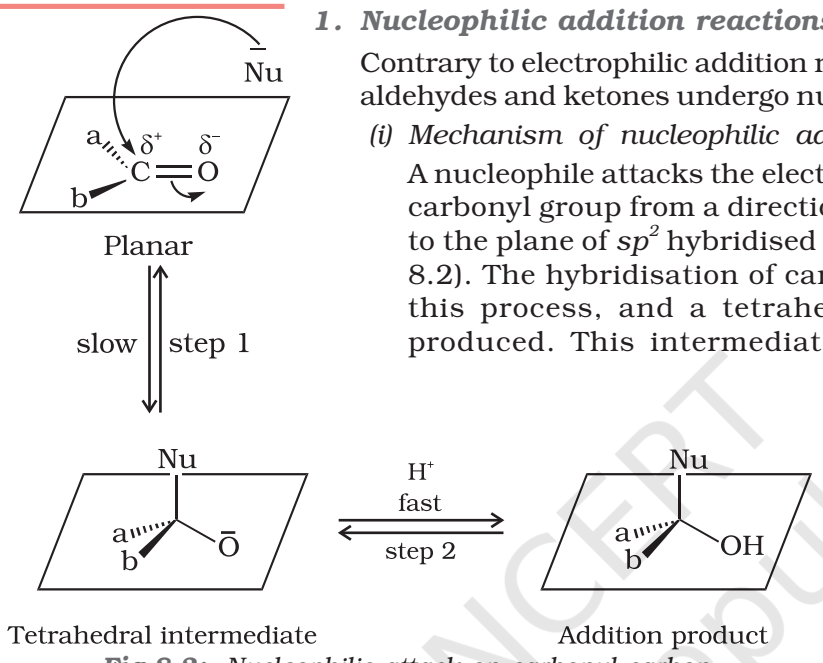


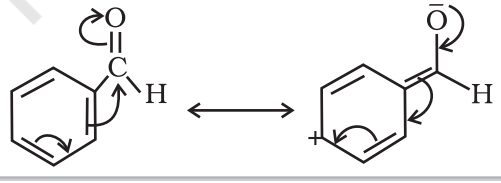
Fig.8.2: *Nucleophilic attack on carbonyl carbon*

(ii) Reactivity

Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl carbon more effectively than in former.

Example 8.3 Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

Solution The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance as shown below and hence it is less reactive than propanal.



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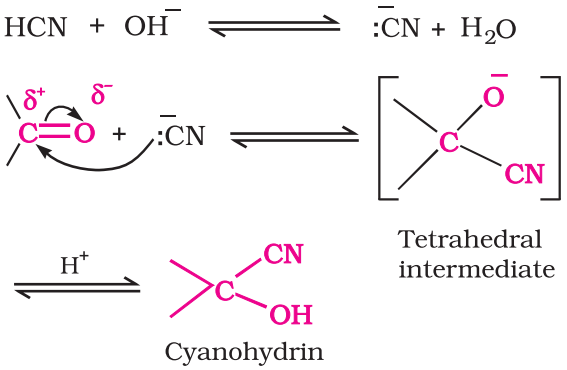
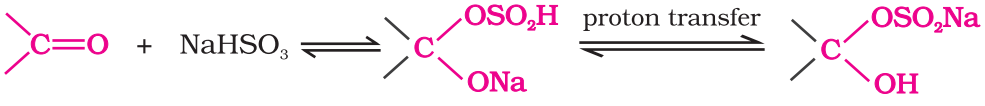
(iii) Some important examples of nucleophilic addition and nucleophilic addition-elimination reactions:



(a) *Addition of hydrogen cyanide (HCN)*: Aldehydes and ketones react with hydrogen cyanide (HCN) to yield cyanohydrins. This reaction occurs very slowly with pure HCN. Therefore, it is catalysed by a base and the generated cyanide ion (CN^-) being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrin.

Cyanohydrins are useful synthetic intermediates.

(b) *Addition of sodium hydrogensulphite:* Sodium hydrogensulphite adds to aldehydes and ketones to form the addition products.

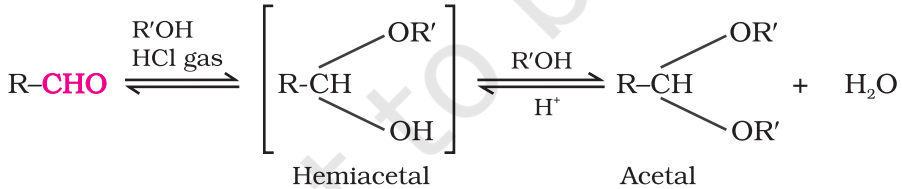


Bisulphite addition compound (crystalline)

The position of the equilibrium lies largely to the right hand side for most aldehydes and to the left for most ketones due to steric reasons. The hydrogensulphite addition compound is water soluble and can be converted back to the original carbonyl compound by treating it with dilute mineral acid or alkali. Therefore, these are useful for separation and purification of aldehydes.

(c) *Addition of Grignard reagents:* (refer Unit 7, Class XII).

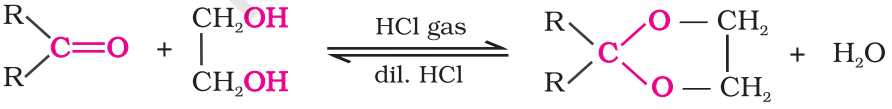
(d) *Addition of alcohols:* Aldehydes react with one equivalent of monohydric alcohol in the presence of dry hydrogen chloride to yield alkoxyalcohol intermediate, known as hemiacetals, which further react with one more molecule of alcohol to give *a gem*-dialkoxy compound known as acetal as shown in the reaction.



Hemiacetal Acetal

Ketones react with ethylene glycol under similar conditions to form cyclic products known as ethylene glycol ketals.

Dry hydrogen chloride protonates the oxygen of the carbonyl compounds and therefore, increases the electrophilicity of the carbonyl carbon facilitating



Ethylene glycol ketal

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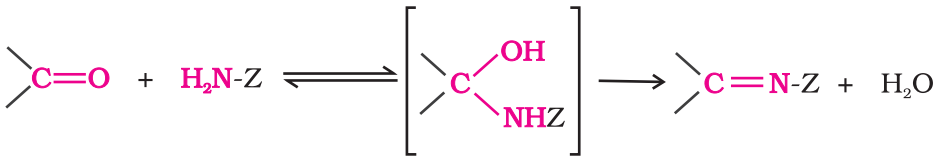
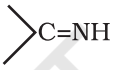
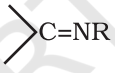
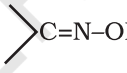
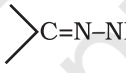
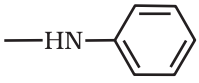
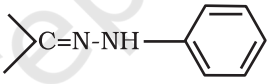
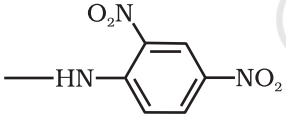
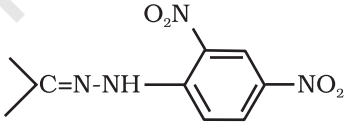
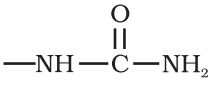
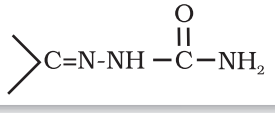
the nucleophilic attack of ethylene glycol. Acetals and ketals are hydrolysed with aqueous mineral acids to yield corresponding aldehydes and ketones respectively.

(e) *Addition of ammonia and its derivatives*: Nucleophiles, such as ammonia and its derivatives H_2N-Z add to the carbonyl group of aldehydes and ketones. The reaction is reversible and catalysed by acid. The equilibrium favours the product formation due to rapid dehydration of the intermediate to form >C=N-Z.



Z = Alkyl, aryl, OH, NH_2, C_6H_5NH, $NHCONH_2$, etc.

Table 8.2: Some N-Substituted Derivatives of Aldehydes and Ketones (>C=N-Z)

Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia		Imine
-R	Amine		Substituted imine (Schiff's base)
—OH	Hydroxylamine		Oxime
$—NH_2$	Hydrazine		Hydrazone
	Phenylhydrazine		Phenylhydrazone
	2,4-Dinitrophenyl-hydrazine		2,4 Dinitrophenyl-hydrazone
	Semicarbazide		Semicarbazone

** 2,4-DNP-derivatives are yellow, orange or red solids, useful for characterisation of aldehydes and ketones.*

2. Reduction

(*i*) *Reduction to alcohols:* Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride ($NaBH_4$) or lithium aluminium hydride ($LiAlH_4$) as well as by catalytic hydrogenation (Unit 7, Class XII).

(*ii*) *Reduction to hydrocarbons:* The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc-amalgam and concentrated hydrochloric acid [**Clemmensen**

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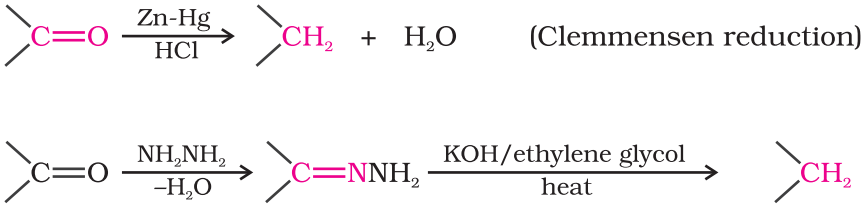
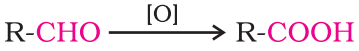
reduction] or with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol (**Wolff-Kishner reduction**).



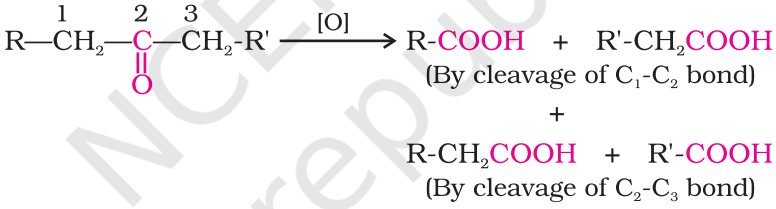
3. Oxidation

Bernhard Tollens (1841-1918) was a Professor of Chemistry at the University of Gottingen, Germany.

Aldehydes differ from ketones in their oxidation reactions. Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, mainly Tollens' reagent and Fehlings' reagent also oxidise aldehydes.



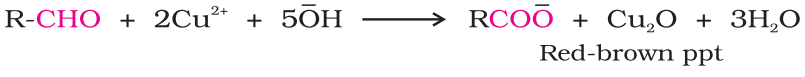
Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage to afford a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.



The mild oxidising agents given below are used to distinguish aldehydes from ketones:

(i) Tollens' test: On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.

(ii) Fehling's test: Fehling reagent comprises of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). These two solutions are mixed in equal amounts before test. On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained. Aldehydes are oxidised to corresponding carboxylate anion. Aromatic aldehydes do not respond to this test.



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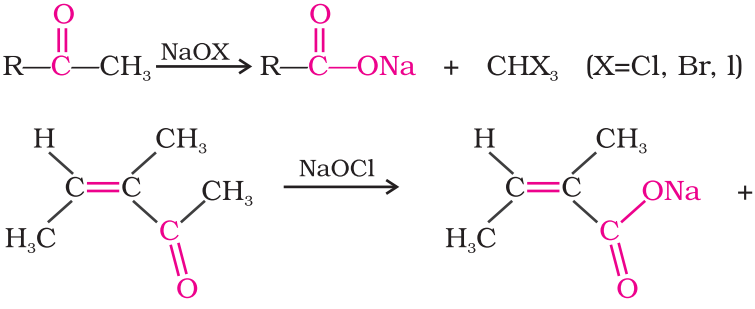
(iii) Oxidation of methyl ketones by haloform reaction: Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted to haloform. This oxidation does not affect a carbon-carbon double bond, if present in the molecule.

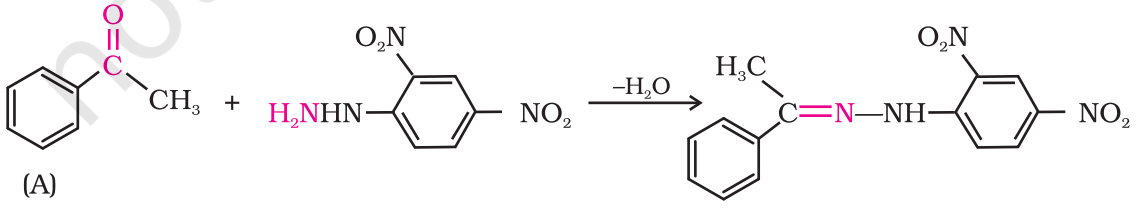


Iodoform reaction with sodium hypoiodite is also used for detection of CH_3CO group or $CH_3CH(OH)$ group which produces CH_3CO group on oxidation.

Example 8.4 An organic compound (A) with molecular formula C_8H_8O forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula $C_7H_6O_2$. Identify the compounds (A) and (B) and explain the reactions involved.

Solution (A) forms 2,4-DNP derivative. Therefore, it is an aldehyde or a ketone. Since it does not reduce Tollens' or Fehling reagent, (A) must be a ketone. (A) responds to iodoform test. Therefore, it should be a methyl ketone. The molecular formula of (A) indicates high degree of unsaturation, yet it does not decolourise bromine water or Baeyer's reagent. This indicates the presence of unsaturation due to an aromatic ring.

Compound (B), being an oxidation product of a ketone should be a carboxylic acid. The molecular formula of (B) indicates that it should be benzoic acid and compound (A) should, therefore, be a monosubstituted aromatic methyl ketone. The molecular formula of (A) indicates that it should be phenyl methyl ketone (acetophenone). Reactions are as follows:



C_8H_8O 2, 4-Dinitrophenylhydrazine 2, 4-DNP derivative

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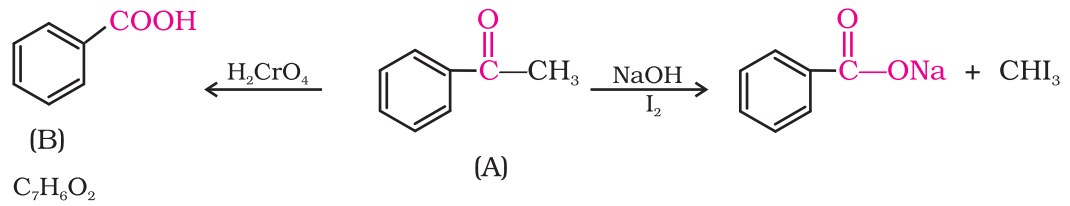
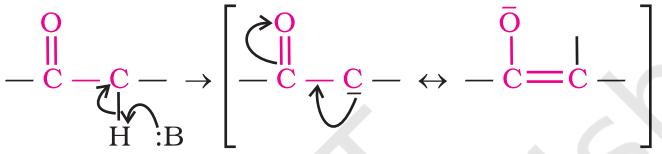


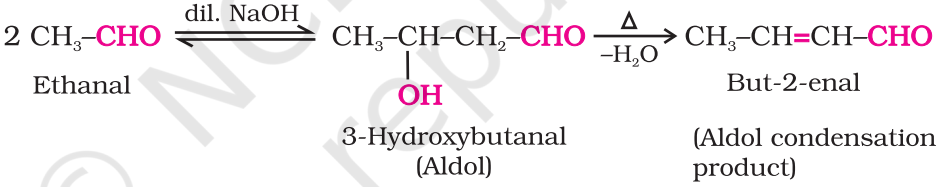
4. *Reactions due to a-hydrogen*

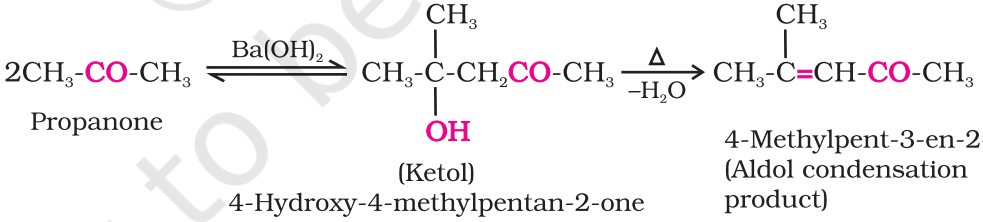
Acidity of α-hydrogens of aldehydes and ketones: The aldehydes and ketones undergo a number of reactions due to the acidic nature of α-hydrogen.

The acidity of α-hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.



(i) Aldol condensation: Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol), respectively. This is known as **Aldol reaction**.





The name aldol is derived from the names of the two functional groups, aldehyde and alcohol, present in the products. The aldol and ketol readily lose water to give α,β-unsaturated carbonyl compounds which are aldol condensation products and the reaction is called **Aldol condensation**. Though ketones give ketols (compounds containing a keto and alcohol groups), the general name aldol condensation still applies to the reactions of ketones due to their similarity with aldehydes.

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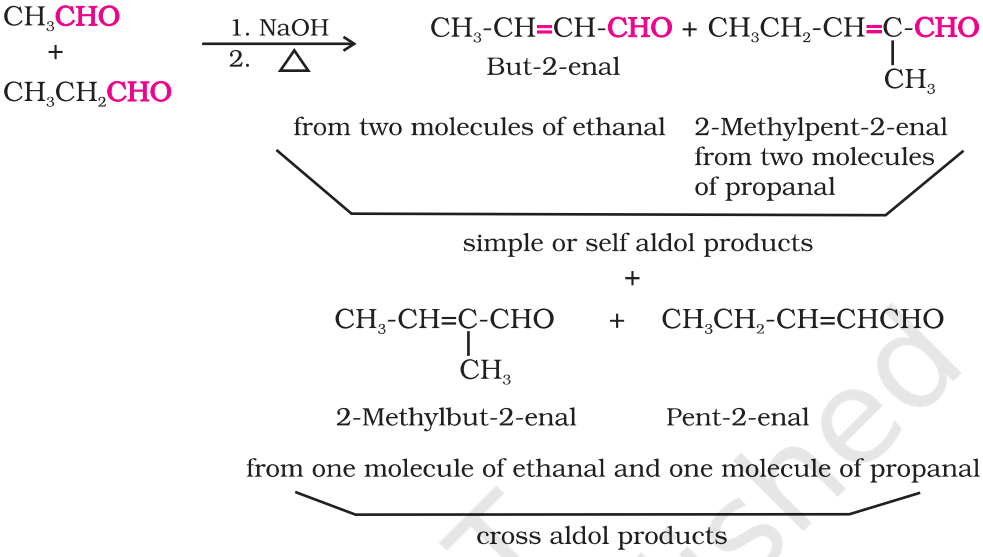
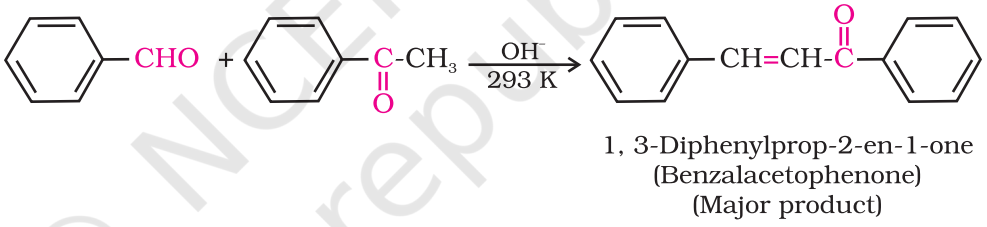
(*ii*) *Cross aldol condensation:* When aldol condensation is carried out between two different aldehydes and / or ketones, it is called **cross aldol condensation**. If both of them contain α-hydrogen atoms, it gives a mixture of four products. This is illustrated below by aldol reaction of a mixture of ethanal and propanal.

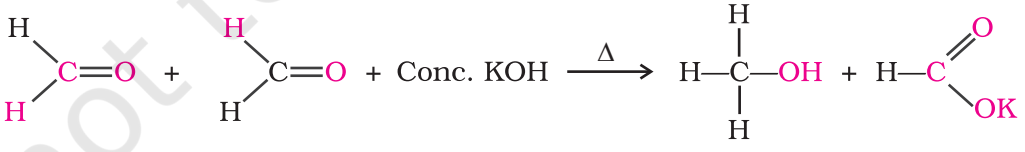


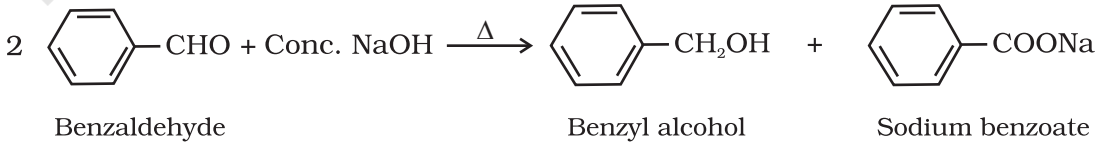
Ketones can also be used as one component in the cross aldol reactions.



5. Other reactions

(*i*) *Cannizzaro reaction:* Aldehydes which do not have an α-hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on heating with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.





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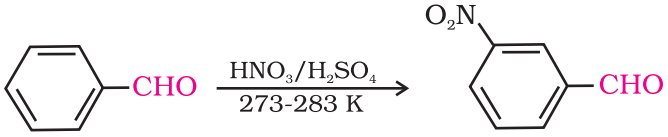
(*ii*) *Electrophilic substitution reaction*: Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and *meta*-directing group.



Benzaldehyde — *m*-Nitrobenzaldehyde

Intext Questions

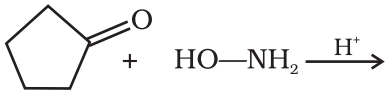
8.4 Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

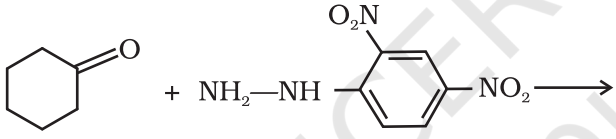
(i) Ethanal, Propanal, Propanone, Butanone.

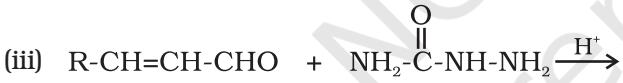
(ii) Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone.

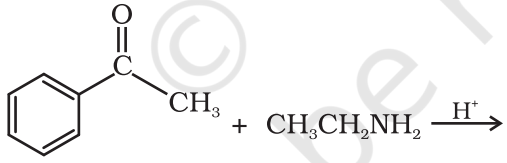
Hint: Consider steric effect and electronic effect.

8.5 Predict the products of the following reactions:

(i) 

(ii) 

(iii) 

(iv) 

8.5 Uses of Aldehydes and Ketones

In chemical industry aldehydes and ketones are used as solvents, starting materials and reagents for the synthesis of other products. Formaldehyde is well known as formalin (40%) solution used to preserve biological specimens and to prepare bakelite (a phenol-formaldehyde resin), urea-formaldehyde glues and other polymeric products. Acetaldehyde is used primarily as a starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs. Benzaldehyde is used in perfumery and in dye industries. Acetone and ethyl methyl ketone are common industrial solvents. Many aldehydes and ketones, e.g., butyraldehyde, vanillin, acetophenone, camphor, etc. are well known for their odours and flavours.

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Carboxylic Acids

Carbon compounds containing a carboxyl functional group, –COOH are called carboxylic acids. The carboxyl group, consists of a *carbonyl* group attached to a *hydroxyl* group, hence its name *carboxyl*. Carboxylic acids may be aliphatic (RCOOH) or aromatic (ArCOOH) depending on the group, alkyl or aryl, attached to carboxylic carbon. Large number of carboxylic acids are found in nature. Some higher members of aliphatic carboxylic acids (C_{12} – C_{18}) known as **fatty acids,** occur in natural fats as esters of glycerol. Carboxylic acids serve as starting material for several other important organic compounds such as anhydrides, esters, acid chlorides, amides, etc.

8.6 Nomenclature and Structure of Carboxyl Group

8.6.1 Nomenclature

Since carboxylic acids are amongst the earliest organic compounds to be isolated from nature, a large number of them are known by their common names. The common names end with the suffix *–ic* acid and have been derived from Latin or Greek names of their natural sources. For example, formic acid (HCOOH) was first obtained from red ants (Latin: *formica* means ant), acetic acid (CH_3COOH) from vinegar (Latin: *acetum*, means vinegar), butyric acid ($CH_3CH_2CH_2COOH$) from rancid butter (Latin: *butyrum,* means butter).

In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending *–e* in the name of the corresponding alkane with *–oic acid*. In numbering the carbon chain, the carboxylic carbon is numbered one. For naming compounds containing more than one carboxyl group, the alkyl chain leaving carboxyl groups is numbered and the number of carboxyl groups is indicated by adding the multiplicative prefix, *dicarboxylic acid*, *tricarboxylic acid,* etc. to the name of parent alkyl chain. The position of –COOH groups are indicated by the arabic numeral before the multiplicative prefix. Some of the carboxylic acids along with their common and IUPAC names are listed in Table 8.3.

Table 8.3 Names and Structures of Some Carboxylic Acids

Structure	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid
HOOC-COOH	Oxalic acid	Ethanedioic acid
HOOC $-CH_2-$COOH	Malonic acid	Propanedioic acid
HOOC $-(CH_2)_2-$COOH	Succinic acid	Butanedioic acid
HOOC $-(CH_2)_3-$COOH	Glutaric acid	Pentanedioic acid
HOOC $-(CH_2)_4-$COOH	Adipic acid	Hexanedioic acid
HOOC $-CH_2-CH(COOH)-CH_2-$COOH	Tricarballylic acid or carballylic acid	Propane-1, 2, 3-tricarboxylic acid

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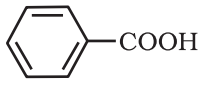
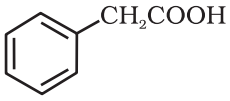
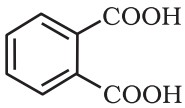
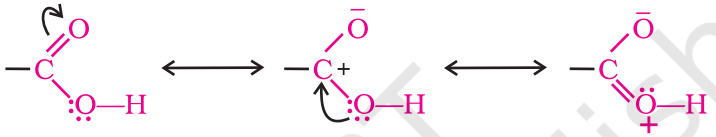
	Benzoic acid	Benzenecarboxylic acid (Benzoic acid)
	Phenylacetic acid	2-Phenylethanoic acid
	Phthalic acid	Benzene-1, 2-dicarboxylic acid

8.6.2 Structure of Carboxyl Group

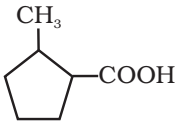
In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°. The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below:

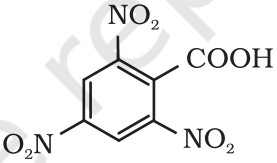


Intext Question

8.6 Give the IUPAC names of the following compounds:

(i) Ph CH_2CH_2COOH (ii) $(CH_3)_2C{=}CHCOOH$

(iii) 

(iv) 

8.7 Methods of Preparation of Carboxylic Acids

Some important methods of preparation of carboxylic acids are as follows.

1. From primary alcohols and aldehydes

Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate ($KMnO_4$) in neutral, acidic or alkaline media or by potassium dichromate ($K_2Cr_2O_7$) and chromium trioxide (CrO_3) in acidic media (Jones reagent).

$$RCH_2OH \xrightarrow[2.\ H_3O^+]{1.\ \text{alkaline } KMnO_4} RCOOH$$

$$\underset{\text{1-Decanol}}{CH_3(CH_2)_8CH_2OH} \xrightarrow[\text{Jones reagent}]{CrO_3\text{-}H_2SO_4} \underset{\text{Decanoic acid}}{CH_3(CH_2)_8COOH}$$

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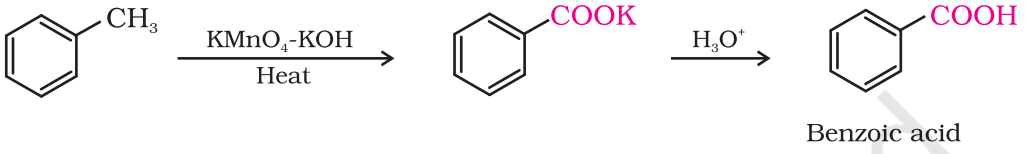
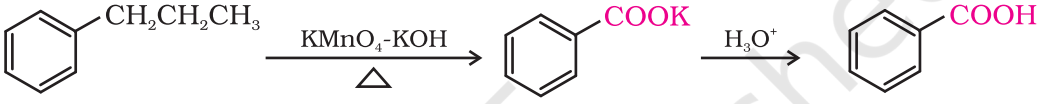
Carboxylic acids are also prepared from aldehydes by the use of mild oxidising agents (Section 8.4).

2. *From alkylbenzenes*

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate. The entire side chain is oxidised to the carboxyl group irrespective of length of the side chain. Primary and secondary alkyl groups are oxidised in this manner while tertiary group is not affected. Suitably substituted alkenes are also oxidised to carboxylic acids with these oxidising reagents.



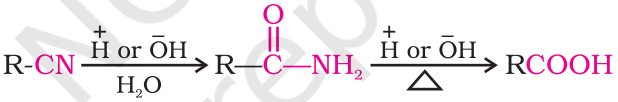
Benzoic acid

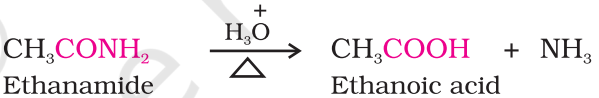


Benzoic acid

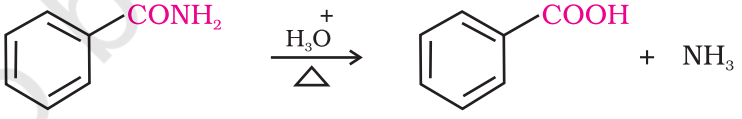
3. *From nitriles and amides*

Nitriles are hydrolysed to amides and then to acids in the presence of H^+ or $\bar{O}H$ as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.





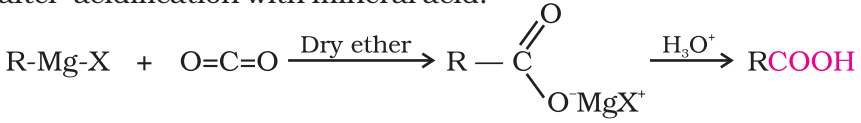
Ethanamide — Ethanoic acid



Benzamide — Benzoic acid

4. *From Grignard reagents*

Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which in turn give corresponding carboxylic acids after acidification with mineral acid.



As we know, the Grignard reagents and nitriles can be prepared from alkyl halides (refer Unit 6, Class XII). The above methods

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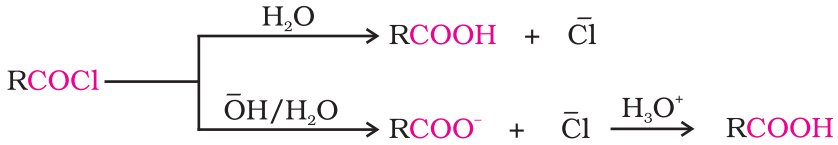
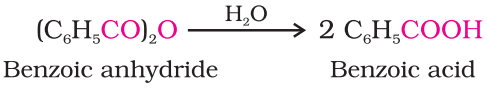
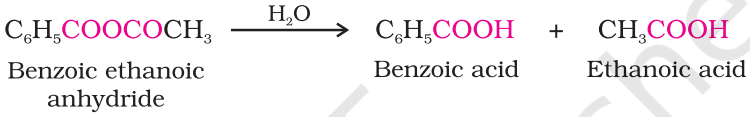
(3 and 4) are useful for converting alkyl halides into corresponding carboxylic acids having one carbon atom more than that present in alkyl halides (ascending the series).

5. *From acyl halides and anhydrides*

Acid chlorides when hydrolysed with water give carboxylic acids or more readily hydrolysed with aqueous base to give carboxylate ions which on acidification provide corresponding carboxylic acids. Anhydrides on the other hand are hydrolysed to corresponding acid(s) with water.

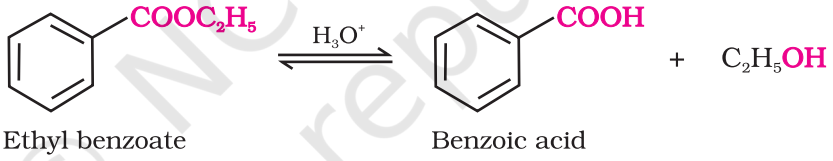


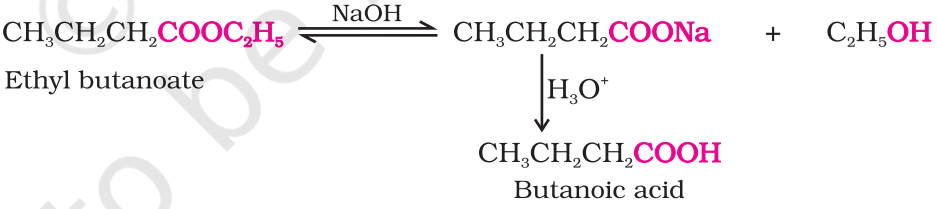




6. *From esters*

Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives carboxylates, which on acidification give corresponding carboxylic acids.





Example 8.5

Write chemical reactions to affect the following transformations:

(i) Butan-1-ol to butanoic acid
(ii) Benzyl alcohol to phenylethanoic acid
(iii) 3-Nitrobromobenzene to 3-nitrobenzoic acid
(iv) 4-Methylacetophenone to benzene-1,4-dicarboxylic acid
(v) Cyclohexene to hexane-1,6-dioic acid
(vi) Butanal to butanoic acid.

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Solution

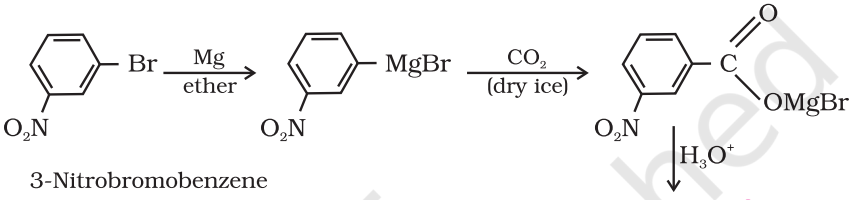
(i) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{Jones reagent}]{CrO_3\text{-}H_2SO_4} CH_3CH_2CH_2COOH$

Butan-1-ol — Butanoic acid

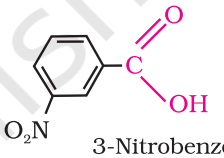
(ii) $C_6H_5CH_2OH \xrightarrow{HBr} C_6H_5CH_2Br \xrightarrow{KCN} C_6H_5CH_2CN \xrightarrow[\triangle]{H_3O^+} C_6H_5CH_2COOH$

Benzyl alcohol — Benzyl bromide — Benzyl cyanide — Phenylethanoic acid

(iii)

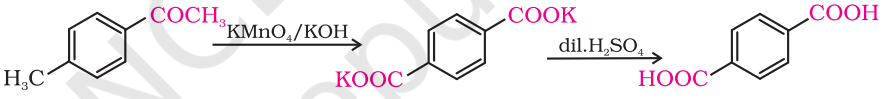


3-Nitrobromobenzene



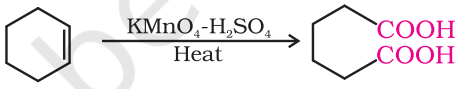
3-Nitrobenzoic acid

(iv)



4-Methylacetophenone — Dipotassium benzene-1, 4-dicarboxylate — Benzene-1, 4-dicarboxylic acid (Terephthalic acid)

(v)



Cyclohexene — Hexane-1, 6-dioic acid (Adipic acid)

(vi) $CH_3CH_2CH_2CHO \xrightarrow[\text{(Tollens' reagent)}]{\text{Ammoniacal } AgNO_3} CH_3CH_2CH_2COOH$

Butanal — Butanoic acid

Intext Question

8.7 Show how each of the following compounds can be converted to benzoic acid.

(i) Ethylbenzene (ii) Acetophenone

(iii) Bromobenzene (iv) Phenylethene (Styrene)

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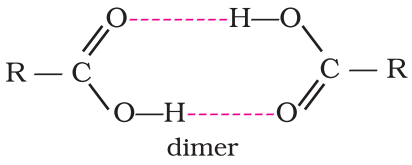
8.8 Physical Properties

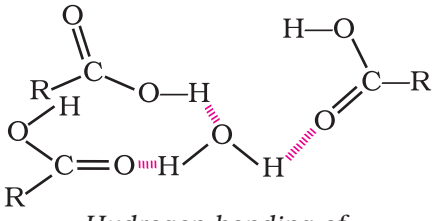
Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids and are practically odourless due to their low volatility. Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.



dimer

In vapour state or in aprotic solvent

Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water. The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part. Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.



Hydrogen bonding of RCOOH with H_2O

8.9 Chemical Reactions

The reaction of carboxylic acids are classified as follows:

8.9.1 Reactions Involving Cleavage of O–H Bond

Acidity

Reactions with metals and alkalies

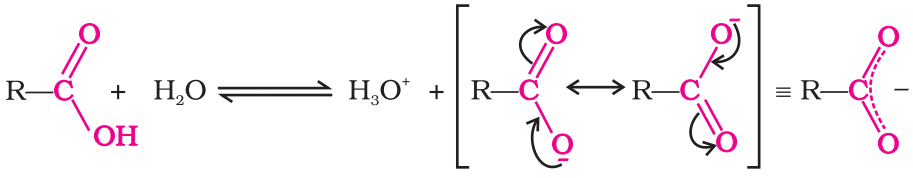
The carboxylic acids like alcohols evolve hydrogen with electropositive metals and form salts with alkalies similar to phenols. However, unlike phenols they react with weaker bases such as carbonates and hydrogencarbonates to evolve carbon dioxide. This reaction is used to detect the presence of carboxyl group in an organic compound.

$$2R\text{-}COOH + 2Na \longrightarrow \underset{\text{Sodium carboxylate}}{2R\text{-}COO^{-}Na^{+}} + H_2$$

$$R\text{-}COOH + NaOH \longrightarrow R\text{-}COO^{-}Na^{+} + H_2O$$

$$R\text{-}COOH + NaHCO_3 \longrightarrow R\text{-}COO^{-}Na^{+} + H_2O + CO_2$$

Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.



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For the above reaction:

$$K_{eq} = \frac{[H_3\overset{+}{O}]\,[RCO\overset{-}{O}]}{[H_2O]\,[RCOOH]} \qquad K_a = K_{eq}\,[H_2O] = \frac{[H_3\overset{+}{O}]\,[RCO\overset{-}{O}]}{[RCOOH]}$$

where K_{eq}, is equilibrium constant and K_a is the acid dissociation constant.

For convenience, the strength of an acid is generally indicated by its pK_a value rather than its K_a value.

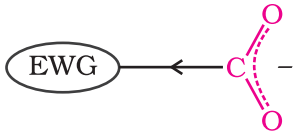
$$pK_a = -\log K_a$$

The pK_a of hydrochloric acid is –7.0, where as pK_a of trifluoroacetic acid (the strongest carboxylic acid), benzoic acid and acetic acid are 0.23, 4.19 and 4.76, respectively.

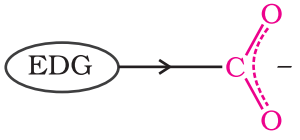
Smaller the pK_a, the stronger the acid (the better it is as a proton donor). Strong acids have pK_a values < 1, the acids with pK_a values between 1 and 5 are considered to be moderately strong acids, weak acids have pK_a values between 5 and 15, and extremely weak acids have pK_a values >15.

Carboxylic acids are weaker than mineral acids, but they are stronger acids than alcohols and many simple phenols (pK_a is ~16 for ethanol and 10 for phenol). In fact, carboxylic acids are amongst the most acidic organic compounds you have studied so far. You already know why phenols are more acidic than alcohols. The higher acidity of carboxylic acids as compared to phenols can be understood similarly. The conjugate base of carboxylic acid, a carboxylate ion, is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. The conjugate base of phenol, a phenoxide ion, has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom. Therefore, resonance in phenoxide ion is not as important as it is in carboxylate ion. Further, the negative charge is delocalised over two electronegative oxygen atoms in carboxylate ion whereas it is less effectively delocalised over one oxygen atom and less electronegative carbon atoms in phenoxide ion (Unit 7, Class XII). Thus, the carboxylate ion is more stabilised than phenoxide ion, so carboxylic acids are more acidic than phenols.

Effect of substituents on the acidity of carboxylic acids: Substituents may affect the stability of the conjugate base and thus, also affect the acidity of the carboxylic acids. Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects. Conversely, electron donating groups decrease the acidity by destabilising the conjugate base.



Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid



Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid

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The effect of the following groups in increasing acidity order is

$$Ph < I < Br < Cl < F < CN < NO_2 < CF_3$$

Thus, the following acids are arranged in order of increasing acidity (based on pK_a values):

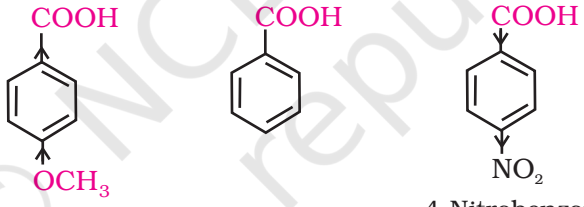
$CF_3COOH > CCl_3COOH > CHCl_2COOH > NO_2CH_2COOH > NC\text{-}CH_2COOH >$ ←

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > HCOOH > ClCH_2CH_2COOH >$ (continue) ←

$C_6H_5COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2COOH$ (continue) ←

Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid, contrary to the decrease expected due to resonance effect shown below:

This is because of greater electronegativity of sp^2 hybridised carbon to which carboxyl carbon is attached. The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.



4-Methoxy benzoic acid (pK_a = 4.46)

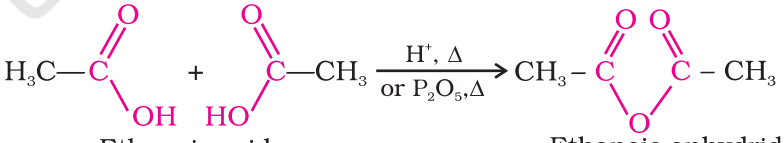
Benzoic acid (pK_a = 4.19)

4-Nitrobenzoic acid (pK_a = 3.41)

8.9.2 Reactions Involving Cleavage of C–OH Bond

1. *Formation of anhydride*

Carboxylic acids on heating with mineral acids such as H_2SO_4 or with P_2O_5 give corresponding anhydride.



Ethanoic acid

Ethanoic anhydride

2. *Esterification*

Carboxylic acids are esterified with alcohols or phenols in the presence of a mineral acid such as concentrated H_2SO_4 or HCl gas as a catalyst.

$$RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$$

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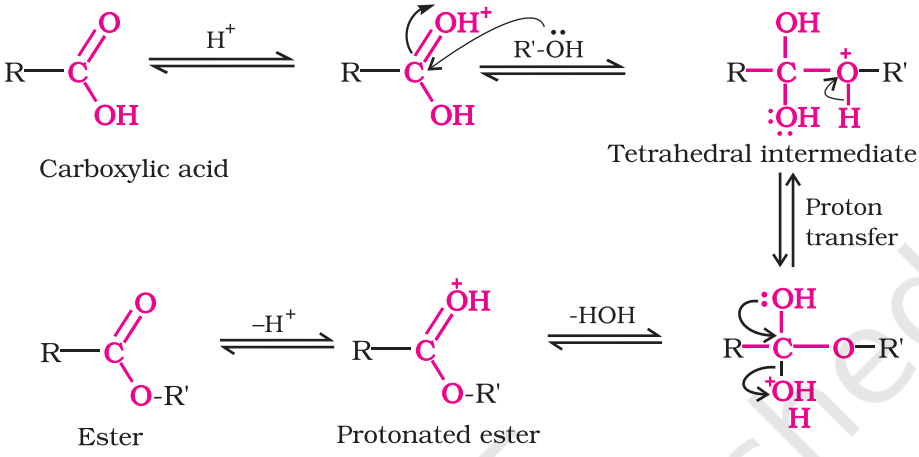
Mechanism of esterification of carboxylic acids: The esterification of carboxylic acids with alcohols is a kind of nucleophilic acyl substitution. Protonation of the carbonyl oxygen activates the carbonyl group towards nucleophilic addition of the alcohol. Proton transfer in the tetrahedral intermediate converts the hydroxyl group into $-^{+}OH_2$ group, which, being a better leaving group, is eliminated as neutral water molecule. The protonated ester so formed finally loses a proton to give the ester.



3. *Reactions with PCl_5, PCl_3 and $SOCl_2$*

The hydroxyl group of carboxylic acids, behaves like that of alcohols and is easily replaced by chlorine atom on treating with PCl_5, PCl_3 or $SOCl_2$. Thionyl chloride ($SOCl_2$) is preferred because the other two products are gaseous and escape the reaction mixture making the purification of the products easier.

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

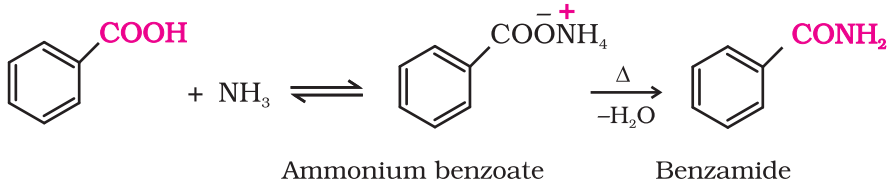
$$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

4. *Reaction with ammonia*

Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature give amides. For example:

$$CH_3COOH + NH_3 \rightleftharpoons \underset{\text{Ammonium acetate}}{CH_3COO^{-}NH_4^{+}} \xrightarrow[-H_2O]{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2}$$



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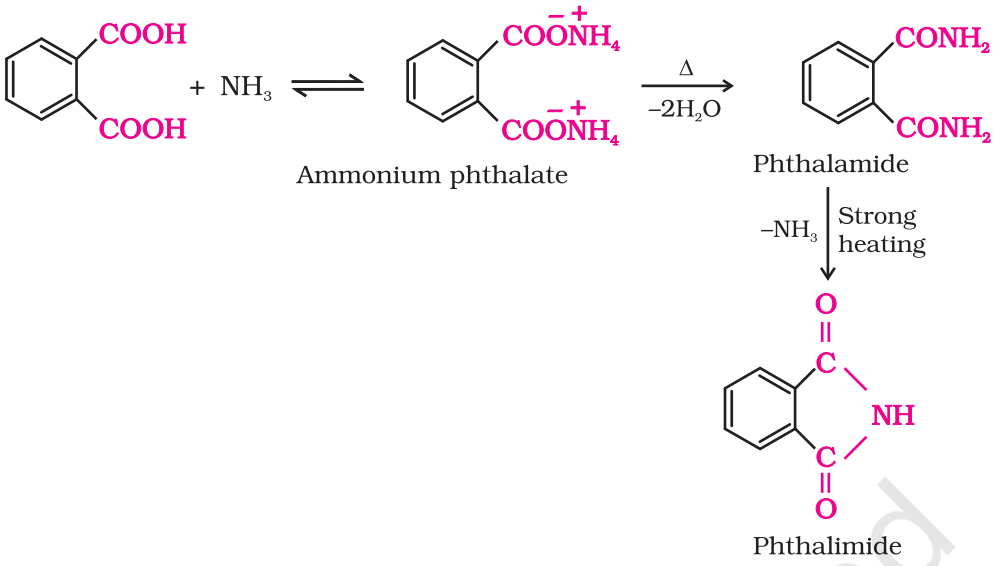

8.9.3 Reactions Involving –COOH Group

1. Reduction

Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride or better with diborane. Diborane does not easily reduce functional groups such as ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.

$$R\text{-}COOH \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4/ether \quad or\ B_2H_6} R\text{-}CH_2OH$$

2. Decarboxylation

Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3 : 1). The reaction is known as decarboxylation.

$$R\text{-}COONa \xrightarrow[Heat]{NaOH\ \&\ CaO} R\text{-}H + Na_2CO_3$$

Alkali metal salts of carboxylic acids also undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid. The reaction is known as **Kolbe electrolysis** (Unit 9, Class XI).

8.9.4 Substitution Reactions in the Hydrocarbon Part

1. Halogenation

Carboxylic acids having an α-hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α-halocarboxylic acids. The reaction is known as **Hell-Volhard-Zelinsky reaction**.

$$R\text{-}CH_2\text{-}COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/Red\ phosphorus} R\text{-}\underset{\displaystyle X}{\underset{|}{CH}}\text{-}COOH$$

X = Cl, Br

α – Halocarboxylic acid

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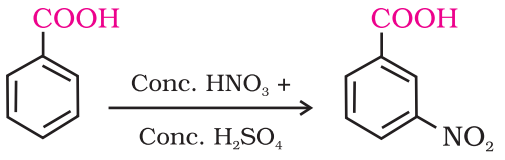
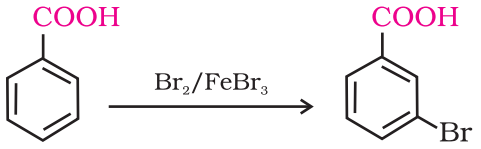
2. *Ring substitution*

Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and meta-directing group. They however, do not undergo **Friedel-Crafts reaction** (because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group).



m-Nitrobenzoic acid



m-Bromobenzoic acid

Intext Question

8.8 Which acid of each pair shown here would you expect to be stronger?

(i) CH_3CO_2H or CH_2FCO_2H (ii) CH_2FCO_2H or CH_2ClCO_2H

(iii) $CH_2FCH_2CH_2CO_2H$ or $CH_3CHFCH_2CO_2H$

(iv) F_3C–C$_6$H$_4$–COOH or H_3C–C$_6$H$_4$–COOH

8.10 Uses of Carboxylic Acids

Methanoic acid is used in rubber, textile, dyeing, leather and electroplating industries. Ethanoic acid is used as solvent and as vinegar in food industry. Hexanedioic acid is used in the manufacture of nylon-6, 6. Esters of benzoic acid are used in perfumery. Sodium benzoate is used as a food preservative. Higher fatty acids are used for the manufacture of soaps and detergents.

Summary

Aldehydes, **ketones** and **carboxylic acids** are some of the important classes of organic compounds containing carbonyl group. These are highly polar molecules. Therefore, they boil at higher temperatures than the hydrocarbons and weakly polar compounds such as ethers of comparable molecular masses. The lower members are more soluble in water because they form hydrogen bonds with water. The higher members, because of large size of hydrophobic chain of carbon atoms, are insoluble in water but soluble in common organic solvents. Aldehydes are prepared by dehydrogenation or controlled oxidation of primary alcohols and controlled or selective reduction of acyl halides. Aromatic aldehydes may also be prepared by oxidation of (i) methylbenzene with chromyl chloride or CrO_3 in the presence of acetic anhydride, (ii) formylation of arenes with carbon monoxide and hydrochloric acid in the presence of anhydrous aluminium chloride, and (iii) cuprous chloride or by hydrolysis of benzal chloride. Ketones are prepared by oxidation of secondary alcohols and hydration of alkynes. Ketones are also prepared by reaction of acyl chloride with dialkylcadmium. A good method for the preparation of aromatic ketones is the **Friedel-Crafts acylation** of aromatic hydrocarbons with acyl chlorides or anhydrides. Both aldehydes and ketones can be prepared by ozonolysis of alkenes. Aldehydes and ketones undergo nucleophilic addition reactions onto the carbonyl group with a number of nucleophiles such as, HCN, $NaHSO_3$, alcohols (or diols),

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ammonia derivatives, and **Grignard reagents**. The α-hydrogens in aldehydes and ketones are acidic. Therefore, aldehydes and ketones having at least one α-hydrogen, undergo A**ldol condensation** in the presence of a base to give α-hydroxyaldehydes (aldol) and α-hydroxyketones(ketol), respectively. Aldehydes having no α-hydrogen undergo **Cannizzaro reaction** in the presence of concentrated alkali. Aldehydes and ketones are reduced to alcohols with $NaBH_4$, $LiAlH_4$, or by catalytic hydrogenation. The carbonyl group of aldehydes and ketones can be reduced to a methylene group by **Clemmensen reduction** or **Wolff-Kishner reduction**. Aldehydes are easily oxidised to carboxylic acids by mild oxidising reagents such as **Tollens' reagent** and **Fehling's reagent**. These oxidation reactions are used to distinguish aldehydes from ketones. Carboxylic acids are prepared by the oxidation of primary alcohols, aldehydes and alkenes by hydrolysis of nitriles, and by treatment of Grignard reagents with carbon dioxide. Aromatic carboxylic acids are also prepared by side-chain oxidation of alkylbenzenes. Carboxylic acids are considerably more acidic than alcohols and most of simple phenols. Carboxylic acids are reduced to primary alcohols with $LiAlH_4$, or better with diborane in ether solution and also undergo α-halogenation with Cl_2 and Br_2 in the presence of red phosphorus (**Hell-Volhard Zelinsky reaction**). Methanal, ethanal, propanone, benzaldehyde, formic acid, acetic acid and benzoic acid are highly useful compounds in industry.

Exercises

8.1 What is meant by the following terms ? Give an example of the reaction in each case.

(i) Cyanohydrin (ii) Acetal (iii) Semicarbazone
(iv) Aldol (v) Hemiacetal (vi) Oxime
(vii) Ketal (vii) Imine (ix) 2,4-DNP-derivative
(x) Schiff's base

8.2 Name the following compounds according to IUPAC system of nomenclature:

(i) $CH_3CH(CH_3)CH_2CH_2CHO$ (ii) $CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl$
(iii) $CH_3CH{=}CHCHO$ (iv) $CH_3COCH_2COCH_3$
(v) $CH_3CH(CH_3)CH_2C(CH_3)_2COCH_3$ (vi) $(CH_3)_3CCH_2COOH$
(vii) $OHCC_6H_4CHO$-*p*

8.3 Draw the structures of the following compounds.

(i) 3-Methylbutanal (ii) *p*-Nitropropiophenone
(iii) *p*-Methylbenzaldehyde (iv) 4-Methylpent-3-en-2-one
(v) 4-Chloropentan-2-one (vi) 3-Bromo-4-phenylpentanoic acid
(vii) *p,p'*-Dihydroxybenzophenone (viii) Hex-2-en-4-ynoic acid

8.4 Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.

(i) $CH_3CO(CH_2)_4CH_3$ (ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$
(iii) $CH_3(CH_2)_5CHO$ (iv) Ph-CH=CH-CHO
(v)

(vi) PhCOPh

8.5 Draw structures of the following derivatives.

(i) The 2,4-dinitrophenylhydrazone of benzaldehyde
(ii) Cyclopropanone oxime
(iii) Acetaldehydedimethylacetal
(iv) The semicarbazone of cyclobutanone
(v) The ethylene ketal of hexan-3-one
(vi) The methyl hemiacetal of formaldehyde

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8.6 Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.
(i) PhMgBr and then H_3O^+ (ii) Tollens' reagent
(iii) Semicarbazide and weak acid (iv) Excess ethanol and acid
(v) Zinc amalgam and dilute hydrochloric acid

8.7 Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.
(i) Methanal (ii) 2-Methylpentanal (iii) Benzaldehyde
(iv) Benzophenone (v) Cyclohexanone (vi) 1-Phenylpropanone
(vii) Phenylacetaldehyde (viii) Butan-1-ol (ix) 2,2-Dimethylbutanal

8.8 How will you convert ethanal into the following compounds?
(i) Butane-1,3-diol (ii) But-2-enal (iii) But-2-enoic acid

8.9 Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as nucleophile and which as electrophile.

8.10 An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

8.11 An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.

8.12 Arrange the following compounds in increasing order of their property as indicated:
(i) Acetaldehyde, Acetone, Di-*tert*-butyl ketone, Methyl *tert*-butyl ketone (reactivity towards HCN)
(ii) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength)
(iii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)

8.13 Give simple chemical tests to distinguish between the following pairs of compounds.
(i) Propanal and Propanone (ii) Acetophenone and Benzophenone
(iii) Phenol and Benzoic acid (iv) Benzoic acid and Ethyl benzoate
(v) Pentan-2-one and Pentan-3-one (vi) Benzaldehyde and Acetophenone
(vii) Ethanal and Propanal

8.14 How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom
(i) Methyl benzoate (ii) *m*-Nitrobenzoic acid
(iii) *p*-Nitrobenzoic acid (iv) Phenylacetic acid
(v) *p*-Nitrobenzaldehyde.

8.15 How will you bring about the following conversions in not more than two steps?
(i) Propanone to Propene (ii) Benzoic acid to Benzaldehyde
(iii) Ethanol to 3-Hydroxybutanal (iv) Benzene to *m*-Nitroacetophenone
(v) Benzaldehyde to Benzophenone (vi) Bromobenzene to 1-Phenylethanol
(vii) Benzaldehyde to 3-Phenylpropan-1-ol
(viii) Benazaldehyde to α-Hydroxyphenylacetic acid
(ix) Benzoic acid to *m*- Nitrobenzyl alcohol

8.16 Describe the following:
(i) Acetylation (ii) Cannizzaro reaction
(iii) Cross aldol condensation (iv) Decarboxylation

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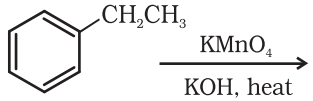
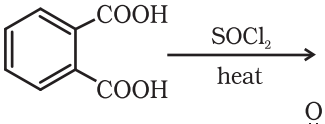
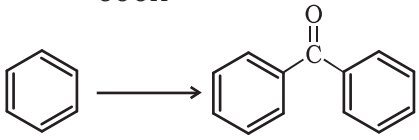
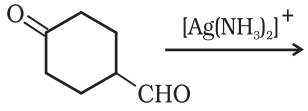
8.17 Complete each synthesis by giving missing starting material, reagent or products

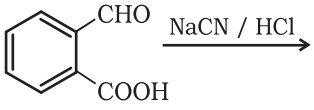
(i) 

(ii) 

(iii) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

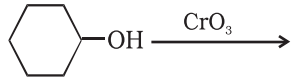
(iv) 

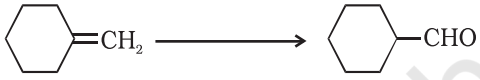
(v) 

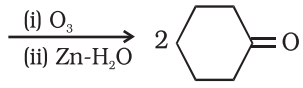
(vi) 

(vii) $C_6H_5CHO + CH_3CH_2CHO \xrightarrow[\Delta]{\text{dil.NaOH}}$

(viii) $CH_3COCH_2COOC_2H_5 \xrightarrow[\text{(ii) } H^+]{\text{(i) } NaBH_4}$

(ix) 

(x) 

(xi) 

8.18 Give plausible explanation for each of the following:

(i) Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.

(ii) There are two $-NH_2$ groups in semicarbazide. However, only one is involved in the formation of semicarbazones.

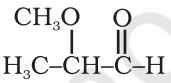
(iii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

8.19 An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

8.20 Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?

Answers to Some Intext Questions

8.1

(i) 

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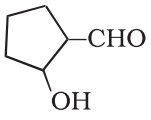
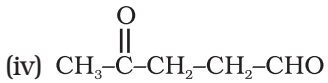
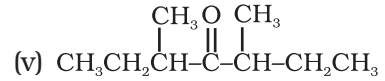
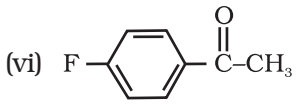
(iii) 

(iv) 

(v) 

(vi) 

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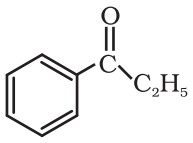
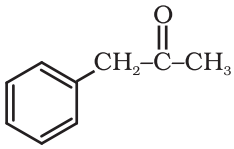
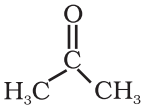
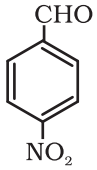
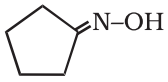
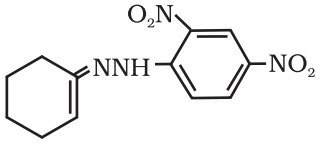
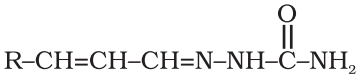
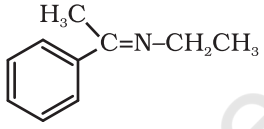
8.2 (i)  (ii)  (iii)  (iv) 

8.3 $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

8.4 (i) Butanone < Propanone < Propanal < Ethanal

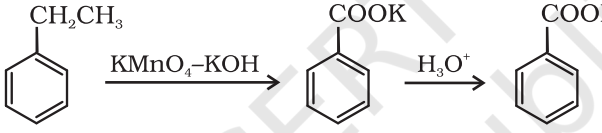
(ii) Acetophenone < *p*-Tolualdehyde , Benzaldehyde < *p*-Nitrobenzaldehyde.

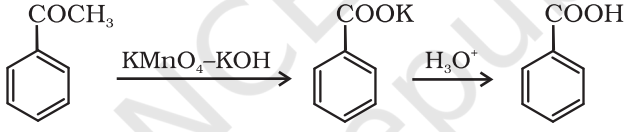
8.5 (i)  (ii) 

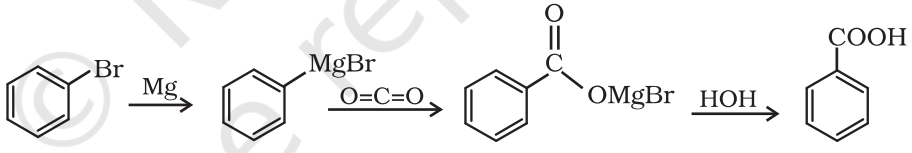
(iii)  (iv) 

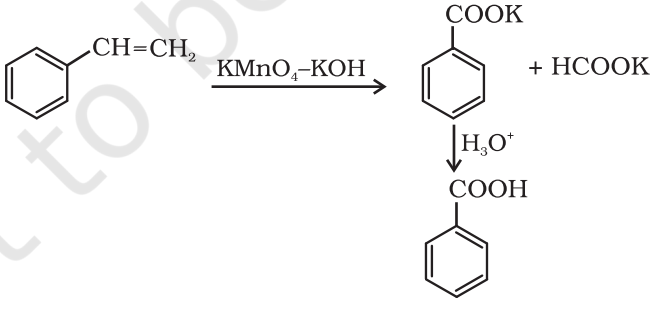
8.6 (i) 3-Phenylpropanoic acid (ii) 3-Methylbut-2-enoic acid

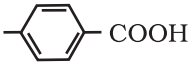
(iii) 2-Methylcyclopentanecarboxylic acid. (iv) 2,4,6-Trinitrobenzoic acid

8.7 (i) 

(ii) 

(iii) 

(iv) 

8.8 (i) CH_2FCOOH (ii) CH_2FCOOH (iii) CH_3CHFCH_2COOH (iv) 

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Unit 9

Amines

Objectives

After studying this Unit, you will be able to

- describe amines as derivatives of ammonia having a pyramidal structure;
- classify amines as primary, secondary and tertiary;
- name amines by common names and IUPAC system;
- describe some of the important methods of preparation of amines;
- explain the properties of amines;
- distinguish between primary, secondary and tertiary amines;
- describe the method of preparation of diazonium salts and their importance in the synthesis of a series of aromatic compounds including azo dyes.

"The chief commercial use of amines is as intermediates in the synthesis of medicines and fibres" .

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl group(s). In nature, they occur among proteins, vitamins, alkaloids and hormones. Synthetic examples include polymers, dye stuffs and drugs. Two biologically active compounds, namely adrenaline and ephedrine, both containing secondary amino group, are used to increase blood pressure. Novocain, a synthetic amino compound, is used as an anaesthetic in dentistry. Benadryl, a well known antihistaminic drug also contains tertiary amino group. Quaternary ammonium salts are used as surfactants. Diazonium salts are intermediates in the preparation of a variety of aromatic compounds including dyes. In this Unit, you will learn about amines and diazonium salts.

9.1 Structure of Amines

I. AMINES

Amines can be considered as derivatives of ammonia, obtained by replacement of one, two or all the three hydrogen atoms by alkyl and/or aryl groups.

For example:

$CH_3–NH_2$, $C_6H_5–NH_2$, $CH_3–NH–CH_3$, $CH_3–N(CH_3)_2$

Like ammonia, nitrogen atom of amines is trivalent and carries an unshared pair of electrons. Nitrogen orbitals in amines are therefore, sp^3 hybridised and the geometry of amines is pyramidal. Each of the three sp^3 hybridised orbitals of nitrogen overlap with orbitals of hydrogen or carbon depending upon the composition of the amines. The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. Due to the presence of unshared pair of electrons, the angle C–N–E, (where E is

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C or H) is less than 109.5°; for instance, it is 108° in case of trimethylamine as shown in Fig. 9.1.

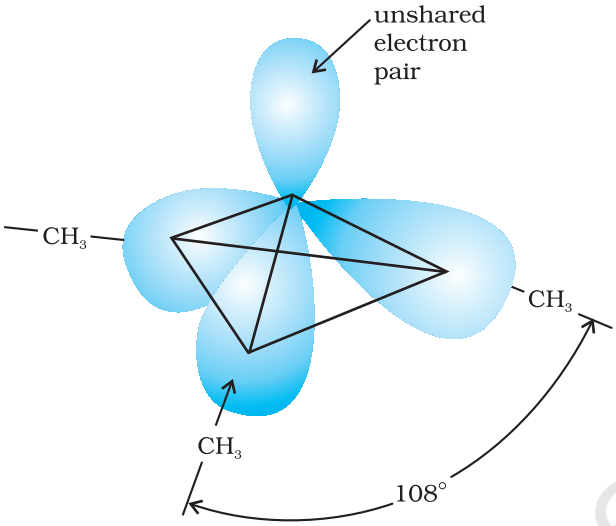
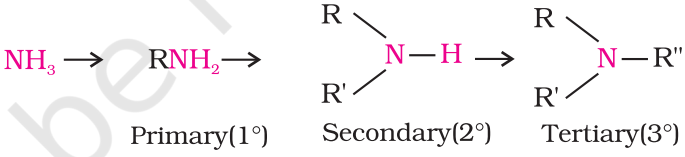


Fig. 9.1 *Pyramidal shape of trimethylamine*

9.2 Classification

Amines are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in ammonia molecule. If one hydrogen atom of ammonia is replaced by R or Ar , we get RNH_2 or $ArNH_2$, a primary amine (1°). If two hydrogen atoms of ammonia or one hydrogen atom of R-NH_2 are replaced by another alkyl/aryl(R') group, what would you get? You get R-NHR', secondary amine. The second alkyl/aryl group may be same or different. Replacement of another hydrogen atom by alkyl/aryl group leads to the formation of tertiary amine. Amines are said to be 'simple' when all the alkyl or aryl groups are the same, and 'mixed' when they are different.



9.3 Nomenclature

In common system, an aliphatic amine is named by prefixing alkyl group to amine, i.e., alkylamine as one word (e.g., methylamine). In secondary and tertiary amines, when two or more groups are the same, the prefix di or tri is appended before the name of alkyl group. In IUPAC system, primary amines are named as **alkanamines**. The name is derived by replacement of 'e' of alkane by the word amine. For example, CH_3NH_2 is named as methanamine. In case, more than one amino group is present at different positions in the parent chain, their positions are specified by giving numbers to the carbon atoms bearing $–NH_2$ groups and suitable prefix such as di, tri, etc. is attached to the amine. The letter 'e' of the suffix of the hydrocarbon part is retained. For example, $H_2N–CH_2–CH_2–NH_2$ is named as ethane-1, 2-diamine.

To name secondary and tertiary amines, we use locant N to designate substituent attached to a nitrogen atom. For example, $CH_3NHCH_2CH_3$ is

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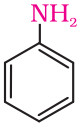
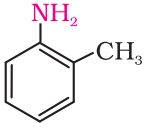
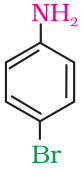
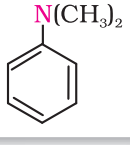
named as N-methylethanamine and $(CH_3CH_2)_3N$ is named as N, N-diethylethanamine. More examples are given in Table 9.1.

In arylamines, $–NH_2$ group is directly attached to the benzene ring. $C_6H_5NH_2$ is the simplest example of arylamine. In common system, it is known as aniline. It is also an accepted IUPAC name. While naming arylamines according to IUPAC system, suffix 'e' of arene is replaced by 'amine'. Thus in IUPAC system, $C_6H_5–NH_2$ is named as benzenamine. Common and IUPAC names of some alkylamines and arylamines are given in Table 9.1.

Table 9.1: Nomenclature of Some Alkylamines and Arylamines

Amine	Common name	IUPAC name
$CH_3–CH_2–NH_2$	Ethylamine	Ethanamine
$CH_3–CH_2–CH_2–NH_2$	*n*-Propylamine	Propan-1-amine
$CH_3–\underset{\displaystyle NH_2}{\underset{\vert}{CH}}–CH_3$	Isopropylamine	Propan-2-amine
$CH_3–\underset{\displaystyle H}{\underset{\vert}{N}}–CH_2–CH_3$	Ethylmethylamine	N-Methylethanamine
$CH_3–\underset{\displaystyle CH_3}{\underset{\vert}{N}}–CH_3$	Trimethylamine	N,N-Dimethylmethanamine
$C_2H_5–\underset{\displaystyle C_2H_5}{\underset{\vert}{N}}–\overset{1}{C}H_2–\overset{2}{C}H_2–\overset{3}{C}H_2–\overset{4}{C}H_3$	*N*,*N*-Diethylbutylamine	N,N-Diethylbutan-1-amine
$NH_2–\overset{1}{C}H_2–\overset{2}{C}H=\overset{3}{C}H_2$	Allylamine	Prop-2-en-1-amine
$NH_2–(CH_2)_6–NH_2$	Hexamethylenediamine	Hexane-1,6-diamine
	Aniline	Aniline or Benzenamine
	*o*-Toluidine	2-Methylaniline
	*p*-Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	*N*,*N*-Dimethylaniline	N,N-Dimethylbenzenamine

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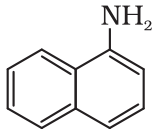
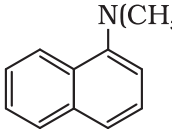
Intext Questions

9.1 Classify the following amines as primary, secondary or tertiary:

(i) 

(ii) 

(iii) $(C_2H_5)_2CHNH_2$ (iv) $(C_2H_5)_2NH$

9.2 (i) Write structures of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$.
(ii) Write IUPAC names of all the isomers.
(iii) What type of isomerism is exhibited by different pairs of amines?

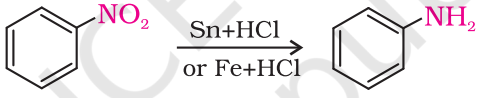
9.4 Preparation of Amines

Amines are prepared by the following methods:

1. Reduction of nitro compounds

Nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum and also by reduction with metals in acidic medium. Nitroalkanes can also be similarly reduced to the corresponding alkanamines.

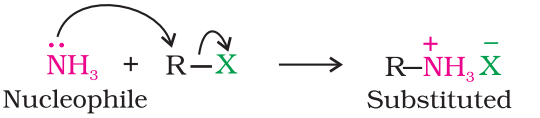
(i)

(ii) 

Reduction with iron scrap and hydrochloric acid is preferred because $FeCl_2$ formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction.

2. Ammonolysis of alkyl halides

You have read (Unit 6, Class XII) that the carbon - halogen bond in alkyl or benzyl halides can be easily cleaved by a nucleophile. Hence, an alkyl or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino ($-NH_2$) group. This process of cleavage of the C–X bond by ammonia molecule is known as **ammonolysis**. The reaction is carried out in a sealed tube at 373 K. The primary amine thus obtained behaves as a nucleophile and can further react with alkyl halide to form secondary and tertiary amines, and finally quaternary ammonium salt.



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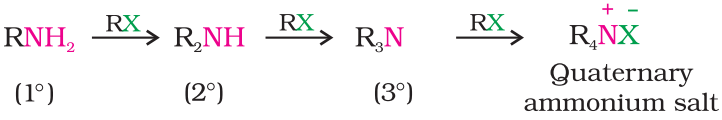
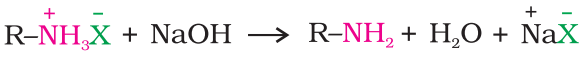


The free amine can be obtained from the ammonium salt by treatment with a strong base:



Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt. However, primary amine is obtained as a major product by taking large excess of ammonia.

The order of reactivity of halides with amines is RI > RBr >RCl.

Example 9.1

Write chemical equations for the following reactions:

(i) Reaction of ethanolic NH_3 with C_2H_5Cl.

(ii) Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of CH_3Cl.

Solution

(i) $C_2H_5–Cl \xrightarrow{NH_3} C_2H_5–NH_2 \xrightarrow{C_2H_5-Cl} C_2H_5–\underset{H}{\overset{|}{N}}–C_2H_5 \xrightarrow{C_2H_5-Cl} C_2H_5–\underset{C_2H_5}{\overset{|}{N}}–C_2H_5 \xrightarrow{C_2H_5Cl} (C_2H_5)_3\overset{+}{N}\,Cl^-$

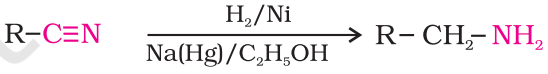
Chloroethane — Ethanamine — N-Ethylethanamine — N,N-Diethylethanamine — Quaternary ammonium Salt

(ii) $C_6H_5–CH_2–Cl \xrightarrow{NH_3} C_6H_5–CH_2NH_2 \xrightarrow{2CH_3Cl} C_6H_5–CH_2–\underset{CH_3}{\overset{|}{N}}–CH_3$

Benzylchloride — Benzylamine — N,N-Dimethylphenylmethanamine

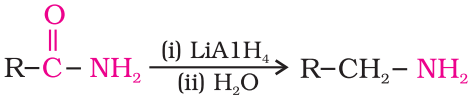
3. Reduction of nitriles

Nitriles on reduction with lithium aluminium hydride ($LiAlH_4$) or catalytic hydrogenation produce primary amines. This reaction is used for ascent of amine series, i.e., for preparation of amines containing one carbon atom more than the starting amine.



4. Reduction of amides

The amides on reduction with lithium aluminium hydride yield amines.



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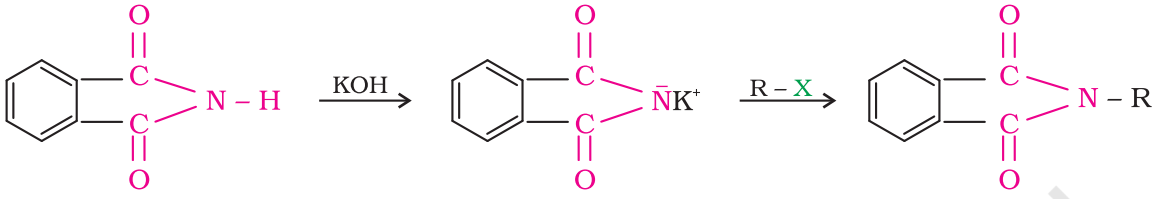
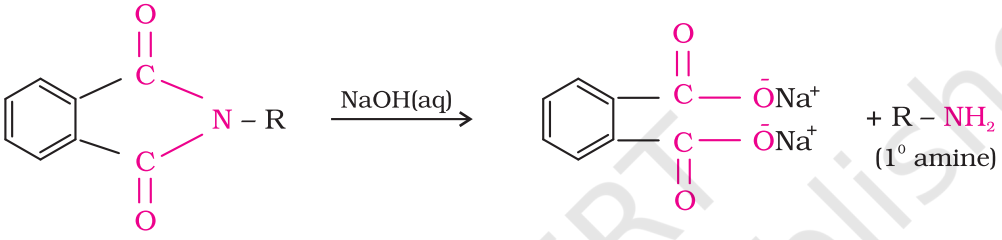
5. *Gabriel phthalimide synthesis*

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

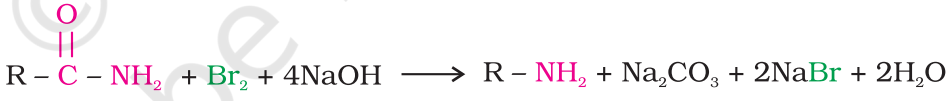


Phthalimide N-Alkylphthalimide



6. *Hoffmann bromamide degradation reaction*

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amine so formed contains one carbon less than that present in the amide.



Example 9.2 Write chemical equations for the following conversions:
(i) $CH_3–CH_2–Cl$ into $CH_3–CH_2–CH_2–NH_2$
(ii) $C_6H_5–CH_2–Cl$ into $C_6H_5–CH_2–CH_2–NH_2$

Solution

(i) $CH_3–CH_2–Cl$ —Ethanolic NaCN→ $CH_3–CH_2–C\equiv N$ —reduction→ $CH_3–CH_2–CH_2–NH_2$

Chloroethane — Propanenitrile — Propan-1-amine

(ii) $C_6H_5–CH_2–Cl$ —Ethanolic NaCN→ $C_6H_5–CH_2–C\equiv N$ —H_2/Ni→ $C_6H_5–CH_2–CH_2–NH_2$

Chlorophenylmethane (Benzyl chloride) — Phenylethanenitrile (Benzyl cyanide) — 2-Phenylethanamine

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Example 9.3

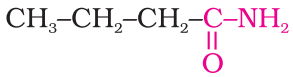
Write structures and IUPAC names of

(i) the amide which gives propanamine by Hoffmann bromamide reaction.

(ii) the amine produced by the Hoffmann degradation of benzamide.

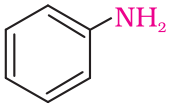
Solution

(i) Propanamine contains three carbons. Hence, the amide molecule must contain four carbon atoms. Structure and IUPAC name of the starting amide with four carbon atoms are given below:



Butanamide

(ii) Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amine formed from benzamide is aromatic primary amine containing six carbon atoms.



Aniline or benzenamine

Intext Question

9.3 How will you convert

(i) Benzene into aniline (ii) Benzene into N, N-dimethylaniline

(iii) $Cl–(CH_2)_4–Cl$ into hexan-1,6-diamine?

9.5 Physical Properties

The lower aliphatic amines are gases with fishy odour. Primary amines with three or more carbon atoms are liquid and still higher ones are solid. Aniline and other arylamines are usually colourless but get coloured on storage due to atmospheric oxidation.

Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part. Higher amines are essentially insoluble in water. Considering the electronegativity of nitrogen of amine and oxygen of alcohol as 3.0 and 3.5 respectively, you can predict the pattern of solubility of amines and alcohols in water. Out of butan-1-ol and butan-1-amine, which will be more soluble in water and why? Amines are soluble in organic solvents like alcohol, ether and benzene. You may remember that alcohols are more polar than amines and form stronger intermolecular hydrogen bonds than amines.

Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen of one and hydrogen of another molecule. This intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it. Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation. Therefore, the order of boiling points of isomeric amines is as follows:

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Primary > Secondary > Tertiary

Intermolecular hydrogen bonding in primary amines is shown in Fig. 9.2.

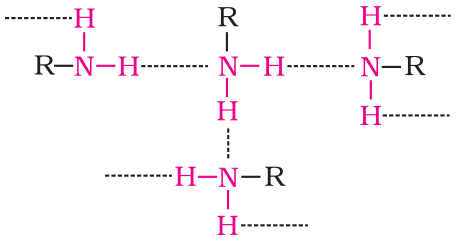


Fig. 9.2 Intermolecular hydrogen bonding in primary amines

Boiling points of amines, alcohols and alkanes of almost the same molar mass are shown in Table 9.2.

Table 9.2: Comparison of Boiling Points of Amines, Alcohols and Alkanes of Similar Molecular Masses

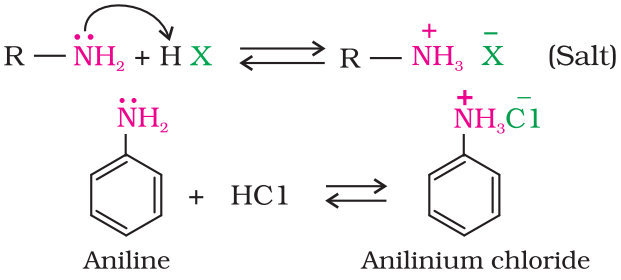
Sl. No.	Compound	Molar mass	b.p./K
1.	n-$C_4H_9NH_2$	73	350.8
2.	$(C_2H_5)_2NH$	73	329.3
3.	$C_2H_5N(CH_3)_2$	73	310.5
4.	$C_2H_5CH(CH_3)_2$	72	300.8
5.	n-C_4H_9OH	74	390.3

9.6 Chemical Reactions

Difference in electronegativity between nitrogen and hydrogen atoms and the presence of unshared pair of electrons over the nitrogen atom makes amines reactive. The number of hydrogen atoms attached to nitrogen atom also decides the course of reaction of amines; that is why primary ($-NH_2$), secondary $\left(\rangle N-H\right)$ and tertiary amines $\left(\rangle N-\right)$ differ in many reactions. Moreover, amines behave as nucleophiles due to the presence of unshared electron pair. Some of the reactions of amines are described below:

1. Basic character of amines

Amines, being basic in nature, react with acids to form salts.



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Amine salts on treatment with a base like NaOH, regenerate the parent amine.

$$R\overset{+}{N}H_3\,\overset{-}{X} + \overset{-}{O}H \longrightarrow R\ddot{N}H_2 + H_2O + \overset{-}{X}$$

Amine salts are soluble in water but insoluble in organic solvents like ether. This reaction is the basis for the separation of amines from the non basic organic compounds insoluble in water.

The reaction of amines with mineral acids to form ammonium salts shows that these are basic in nature. Amines have an unshared pair of electrons on nitrogen atom due to which they behave as **Lewis base.** Basic character of amines can be better understood in terms of their K_b and pK_b values as explained below:

$$R - NH_2 + H_2O \rightleftharpoons R - \overset{+}{N}H_3 + \overset{-}{O}H$$

$$K = \frac{\left[R - \overset{+}{N}H_3\right]\left[\overset{-}{O}H\right]}{[R - NH_2][H_2O]}$$

$$\text{or } K[H_2O] = \frac{\left[R - \overset{+}{N}H_3\right]\left[\overset{-}{O}H\right]}{[R - NH_2]}$$

$$\text{or } K_b = \frac{\left[R - \overset{+}{N}H_3\right]\left[\overset{-}{O}H\right]}{[R - NH_2]}$$

$$pK_b = -\log K_b$$

Larger the value of K_b or smaller the value of pK_b, stronger is the base. The pK_b values of few amines are given in Table 9.3.

pK_b value of ammonia is 4.75. Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups leading to high electron density on the nitrogen atom. Their pK_b values lie in the range of 3 to 4.22. On the other hand, aromatic amines are weaker bases than ammonia due to the electron withdrawing nature of the aryl group.

Table 9.3: pK_b Values of Amines in Aqueous Phase

Name of amine	pK_b
Methanamine	3.38
N-Methylmethanamine	3.27
N,*N*-Dimethylmethanamine	4.22
Ethanamine	3.29
N-Ethylethanamine	3.00
N,*N*-Diethylethanamine	3.25
Benzenamine	9.38
Phenylmethanamine	4.70
N-Methylaniline	9.30
N,*N*-Dimethylaniline	8.92

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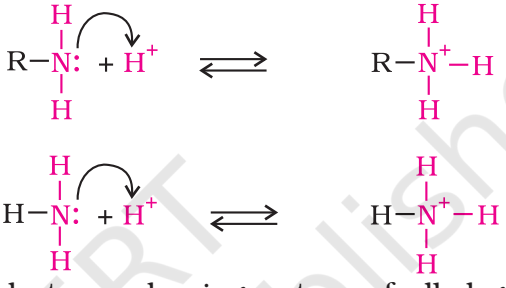
You may find some discrepancies while trying to interpret the K_b values of amines on the basis of +I or –I effect of the substituents present in amines. Besides inductive effect, there are other effects like solvation effect, steric hinderance, etc., which affect the basic strength of amines. Just ponder over. You may get the answer in the following paragraphs.

Structure-basicity relationship of amines

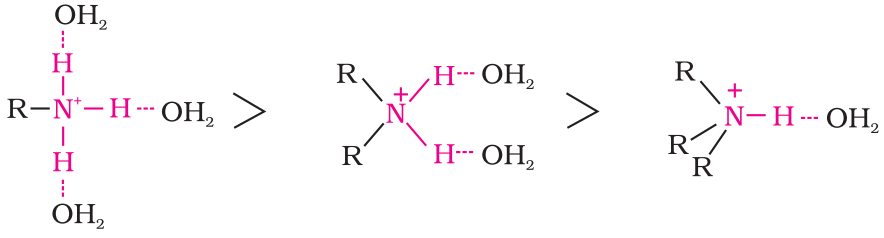
Basicity of amines is related to their structure. Basic character of an amine depends upon the ease of formation of the cation by accepting a proton from the acid. The more stable the cation is relative to the amine, more basic is the amine.

(a) Alkanamines versus ammonia

Let us consider the reaction of an alkanamine and ammonia with a proton to compare their basicity.



Due to the electron releasing nature of alkyl group, it pushes electrons towards nitrogen and thus makes the unshared electron pair more available for sharing with the proton of the acid. Moreover, the substituted ammonium ion formed from the amine gets stabilised due to dispersal of the positive charge by the +I effect of the alkyl group. Hence, alkylamines are stronger bases than ammonia. Thus, the basic nature of aliphatic amines should increase with increase in the number of alkyl groups. This trend is followed in the gaseous phase. The order of basicity of amines in the gaseous phase follows the expected order: tertiary amine > secondary amine > primary amine > NH_3. The trend is not regular in the aqueous state as evident by their pK_b values given in Table 9.3. In the aqueous phase, the substituted ammonium cations get stabilised not only by electron releasing effect of the alkyl group (+I) but also by solvation with water molecules. The greater the size of the ion, lesser will be the solvation and the less stabilised is the ion. The order of stability of ions are as follows:



1° 2° 3°

Decreasing order of extent of H-bonding in water and order of stability of ions by solvation.

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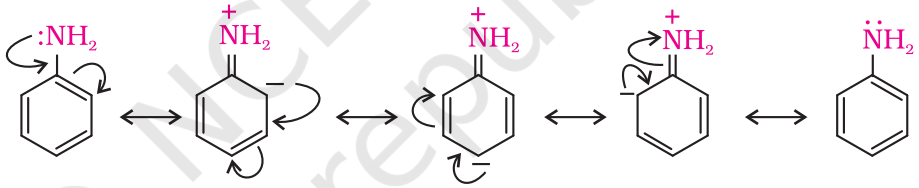
Greater is the stability of the substituted ammonium cation, stronger should be the corresponding amine as a base. Thus, the order of basicity of aliphatic amines should be: primary > secondary > tertiary, which is opposite to the inductive effect based order. Secondly, when the alkyl group is small, like $-CH_3$ group, there is no steric hindrance to H-bonding. In case the alkyl group is bigger than CH_3 group, there will be steric hinderance to H-bonding. Therefore, the change of nature of the alkyl group, e.g., from $-CH_3$ to $-C_2H_5$ results in change of the order of basic strength. Thus, there is a subtle interplay of the inductive effect, solvation effect and steric hinderance of the alkyl group which decides the basic strength of alkyl amines in the aqueous state. The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows:

$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

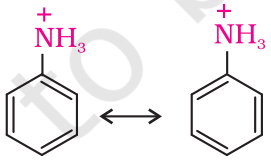
(b) Arylamines versus ammonia

pK_b value of aniline is quite high. Why is it so? It is because in aniline or other arylamines, the $-NH_2$ group is attached directly to the benzene ring. It results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation. If you write different resonating structures of aniline, you will find that aniline is a resonance hybrid of the following five structures.



I II III IV V

On the other hand, anilinium ion obtained by accepting a proton can have only two resonating structures (kekule).



I II

We know that greater the number of resonating structures, greater is the stability. Thus you can infer that aniline (five resonating structures) is more stable than anilinium ion. Hence, the proton acceptability or the basic nature of aniline or other aromatic amines would be less than that of ammonia. In case of substituted aniline, it is observed that electron releasing groups like $-OCH_3$, $-CH_3$ increase basic strength whereas electron withdrawing groups like $-NO_2$, $-SO_3H$, $-COOH$, $-X$ decrease it.

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Example 9.4 Arrange the following in decreasing order of their basic strength:
$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3

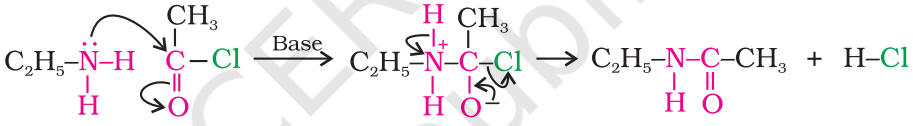
Solution The decreasing order of basic strength of the above amines and ammonia follows the following order:
$(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > C_6H_5NH_2$

2. Alkylation

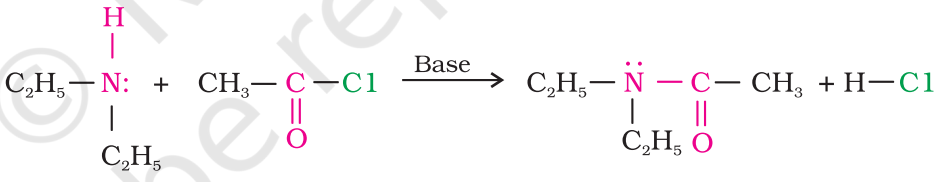
Amines undergo alkylation on reaction with alkyl halides (refer Unit 6, Class XII).

3. Acylation

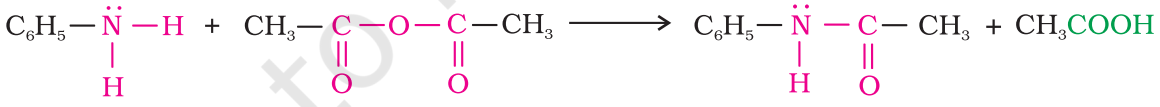
Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. This reaction is known as acylation. You can consider this reaction as the replacement of hydrogen atom of $-NH_2$ or >N–H group by the acyl group. The products obtained by acylation reaction are known as amides. The reaction is carried out in the presence of a base stronger than the amine, like pyridine, which removes HCl so formed and shifts the equilibrium to the right hand side.



Ethanamine — N-Ethylethanamide



N-Ethylethanamine — N,N-Diethylethanamide



Benzenamine — Ethanoic anhydride — N-Phenylethanamide or Acetanilide

Amines also react with benzoyl chloride (C_6H_5COCl). This reaction is known as benzoylation.

$$CH_3NH_2 + C_6H_5COCl \rightarrow CH_3NHCOC_6H_5 + HCl$$

Methanamine — Benzoyl chloride — N – Methylbenzamide

What do you think is the product of the reaction of amines with carboxylic acids ? They form salts with amines at room temperature.

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4. *Carbylamine reaction*

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as **carbylamine reaction** or **isocyanide test** and is used as a test for primary amines.

$$R{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Heat}} R{-}NC + 3KCl + 3H_2O$$

5. *Reaction with nitrous acid*

Three classes of amines react differently with nitrous acid which is prepared *in situ* from a mineral acid and sodium nitrite.

(a) Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively and alcohols. Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.

$$R{-}NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R{-}\overset{+}{N}_2\overset{-}{Cl}] \xrightarrow{H_2O} ROH + N_2 + HCl$$

(b) Aromatic amines react with nitrous acid at low temperatures (273-278 K) to form diazonium salts, a very important class of compounds used for synthesis of a variety of aromatic compounds discussed in Section 9.7.

$$C_6H_5{-}NH_2 \xrightarrow[273 - 278\ K]{NaNO_2 + 2HCl} C_6H_5{-}\overset{+}{N}_2\overset{-}{Cl} + NaCl + 2H_2O$$

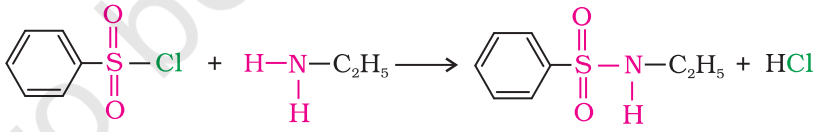
Aniline — Benzenediazonium chloride

Secondary and tertiary amines react with nitrous acid in a different manner.

6. *Reaction with arylsulphonyl chloride*

Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), which is also known as **Hinsberg's reagent,** reacts with primary and secondary amines to form sulphonamides.

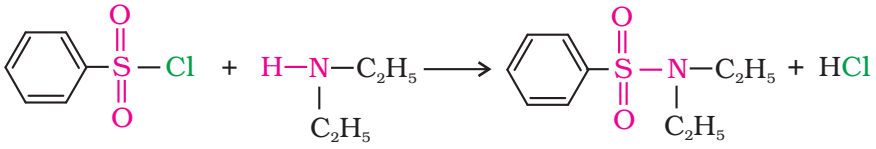
(a) The reaction of benzenesulphonyl chloride with primary amine yields N-ethylbenzenesulphonyl amide.



N-Ethylbenzenesulphonamide
(soluble in alkali)

The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

(b) In the reaction with secondary amine, N,N-diethyl-benzenesulphonamide is formed.



N,N-Diethylbenzenesulphonamide

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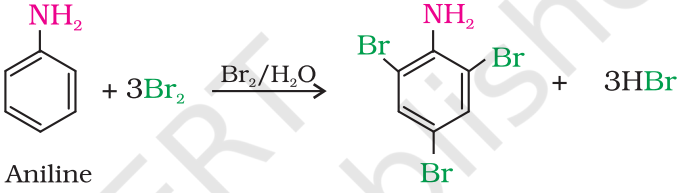
Since N, N-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

(c) Tertiary amines do not react with benzenesulphonyl chloride. This property of amines reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines. However, these days benzenesulphonyl chloride is replaced by *p*-toluenesulphonyl chloride.

7. *Electrophilic substitution*

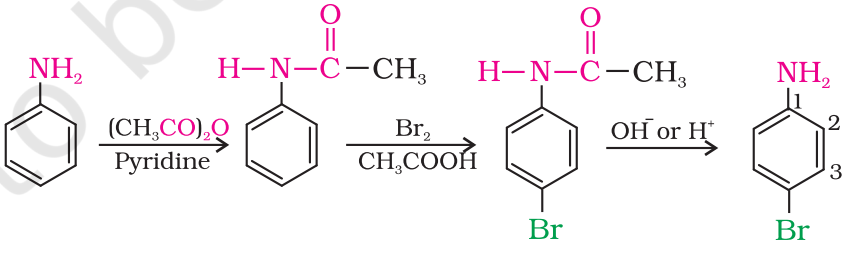
You have read earlier that aniline is a resonance hybrid of five structures. Where do you find the maximum electron density in these structures? *Ortho*- and *para*-positions to the $-NH_2$ group become centres of high electron density. Thus $-NH_2$ group is *ortho* and *para* directing and a powerful activating group.

(a) Bromination: Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline.



Aniline — 2,4,6-Tribromoaniline

The main problem encountered during electrophilic substitution reactions of aromatic amines is that of their very high reactivity. Substitution tends to occur at *ortho*- and *para*-positions. If we have to prepare monosubstituted aniline derivative, how can the activating effect of $-NH_2$ group be controlled ? This can be done by protecting the $-NH_2$ group by acetylation with acetic anhydride, then carrying out the desired substitution followed by hydrolysis of the substituted amide to the substituted amine.



Aniline — *N*-Phenylethanamide (Acetanilide) — (Major) — 4-Bromoaniline

The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below:

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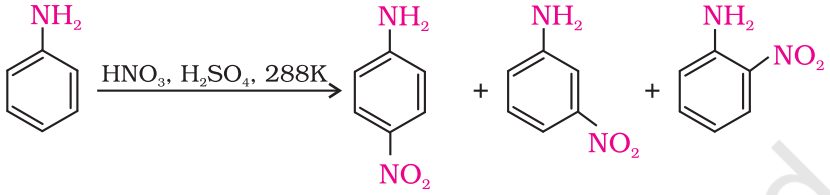
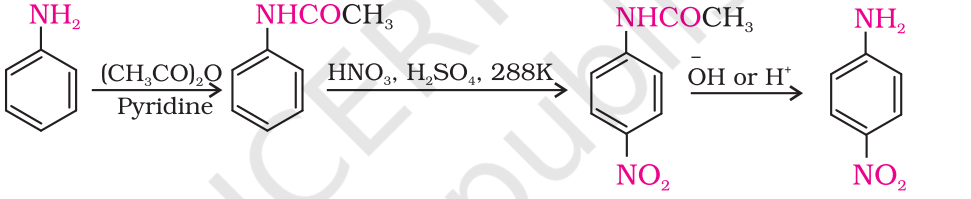
Hence, the lone pair of electrons on nitrogen is less available for donation to benzene ring by resonance. Therefore, activating effect of $-NHCOCH_3$ group is less than that of amino group.

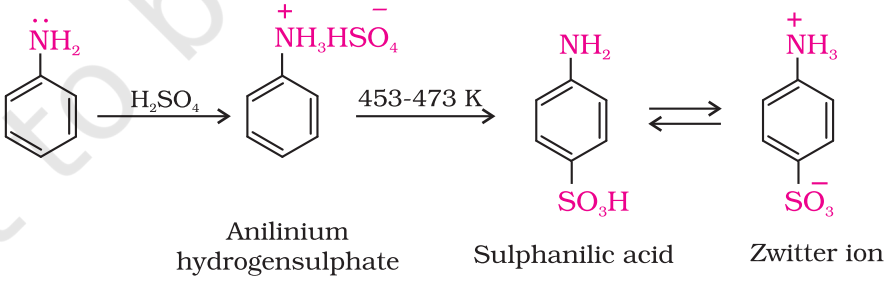
(b) *Nitration:* Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives. Moreover, in the strongly acidic medium, aniline is protonated to form the anilinium ion which is *meta* directing. That is why besides the *ortho* and *para* derivatives, significant amount of *meta* derivative is also formed.



However, by protecting the $-NH_2$ group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the *p*-nitro derivative can be obtained as the major product.



(c) *Sulphonation:* Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate which on heating with sulphuric acid at 453-473K produces p-aminobenzene sulphonic acid, commonly known as sulphanilic acid, as the major product.



Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.

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Intext Questions

9.4 Arrange the following in increasing order of their basic strength:
(i) $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$ and $(C_2H_5)_2NH$
(ii) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, $C_6H_5NH_2$
(iii) CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$.

9.5 Complete the following acid-base reactions and name the products:
(i) $CH_3CH_2CH_2NH_2 + HCl \rightarrow$ (ii) $(C_2H_5)_3N + HCl \rightarrow$

9.6 Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

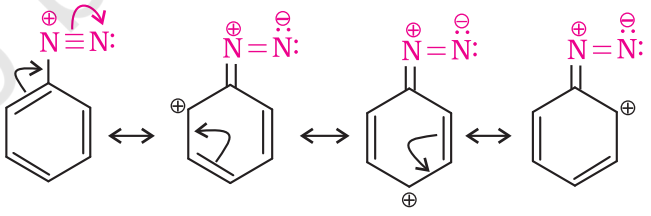
9.7 Write chemical reaction of aniline with benzoyl chloride and write the name of the product obtained.

9.8 Write structures of different isomers corresponding to the molecular formula, C_3H_9N. Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

II. DIAZONIUM SALTS

The diazonium salts have the general formula $RN_2^+X^-$ where R stands for an aryl group and X^- ion may be Cl^- Br^-, HSO_4^-, BF_4^-, etc. They are named by suffixing diazonium to the name of the parent hydrocarbon from which they are formed, followed by the name of anion such as chloride, hydrogensulphate, etc. The N_2^+ group is called diazonium group. For example, $C_6H_5N_2^+Cl^-$ is named as benzenediazonium chloride and $C_6H_5N_2^+HSO_4^-$ is known as benzenediazonium hydrogensulphate.

Primary aliphatic amines form highly unstable alkyldiazonium salts (refer to Section 9.6). Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperatures (273-278 K). The stability of arenediazonium ion is explained on the basis of resonance.



9.7 Method of Preparation of Diazonium Salts

Benzenediazonium chloride is prepared by the reaction of aniline with nitrous acid at 273-278K. Nitrous acid is produced in the reaction mixture by the reaction of sodium nitrite with hydrochloric acid. The conversion of primary aromatic amines into diazonium salts is known as **diazotisation**. Due to its instability, the diazonium salt is not generally stored and is used immediately after its preparation.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$$

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9.8 Physical Properties

Benzenediazonium chloride is a colourless crystalline solid. It is readily soluble in water and is stable in cold but reacts with water when warmed. It decomposes easily in the dry state. Benzenediazonium fluoroborate is water insoluble and stable at room temperature.

9.9 Chemical Reactions

The reactions of diazonium salts can be broadly divided into two categories, namely (A) reactions involving displacement of nitrogen and (B) reactions involving retention of diazo group.

A. Reactions involving displacement of nitrogen

Diazonium group being a very good leaving group, is substituted by other groups such as Cl^-, Br^-, I^-, CN^- and OH^- which displace nitrogen from the aromatic ring. The nitrogen formed escapes from the reaction mixture as a gas.

1. *Replacement by halide or cyanide ion*: The Cl^-, Br^- and CN^- nucleophiles can easily be introduced in the benzene ring in the presence of Cu(I) ion. This reaction is called **Sandmeyer reaction**.

$$ArN_2^+X^- \xrightarrow{Cu_2Cl_2/HCl} ArCl + N_2$$
$$ArN_2^+X^- \xrightarrow{Cu_2Br_2/HBr} ArBr + N_2$$
$$ArN_2^+X^- \xrightarrow{CuCN/KCN} ArCN + N_2$$

Alternatively, chlorine or bromine can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder. This is referred as **Gatterman reaction**.

$$ArN_2^+X^- \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$$
$$ArN_2^+X^- \xrightarrow{Cu/HBr} ArBr + N_2 + CuX$$

The yield in Sandmeyer reaction is found to be better than Gattermann reaction.

2. *Replacement by iodide ion*: Iodine is not easily introduced into the benzene ring directly, but, when the diazonium salt solution is treated with potassium iodide, iodobenzene is formed.

$$ArN_2^+Cl^- + KI \longrightarrow ArI + KCl + N_2$$

3. *Replacement by fluoride ion*: When arenediazonium chloride is treated with fluoroboric acid, arene diazonium fluoroborate is precipitated which on heating decomposes to yield aryl fluoride.

$$ArN_2^+Cl^- + HBF_4 \longrightarrow Ar-N_2^+BF_4^- \xrightarrow{\Delta} Ar-F + BF_3 + N_2$$

4. *Replacement by H*: Certain mild reducing agents like hypophosphorous acid (phosphinic acid) or ethanol reduce diazonium salts to arenes and themselves get oxidised to phosphorous acid and ethanal, respectively.

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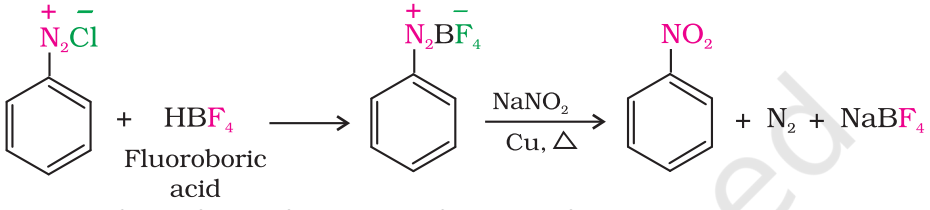
$$ArN_2^+Cl^- + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$$

$$ArN_2^+Cl^- + CH_3CH_2OH \longrightarrow ArH + N_2 + CH_3CHO + HCl$$

5. *Replacement by hydroxyl group*: If the temperature of the diazonium salt solution is allowed to rise upto 283 K, the salt gets hydrolysed to phenol.

$$ArN_2^+Cl^- + H_2O \longrightarrow ArOH + N_2 + HCl$$

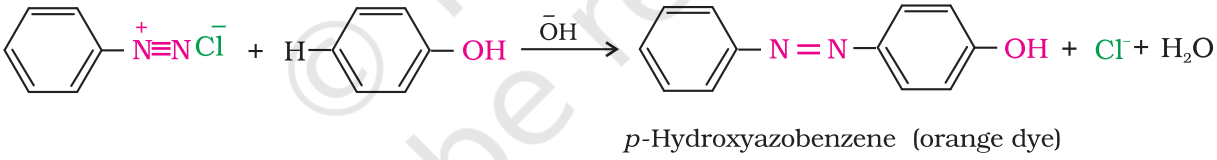
6. *Replacement by $-NO_2$ group*: When diazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by $-NO_2$ group.



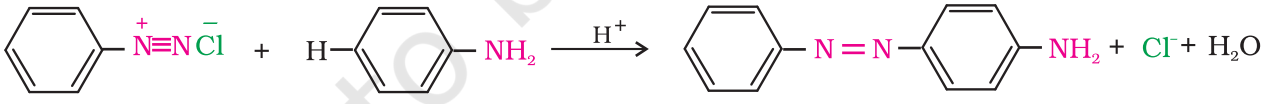
B. Reactions involving retention of diazo group

coupling reactions

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the –N=N– bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form *p*-hydroxyazobenzene. This type of reaction is known as coupling reaction. Similarly the reaction of diazonium salt with aniline yields *p*-aminoazobenzene. This is an example of electrophilic substitution reaction.



p-Hydroxyazobenzene (orange dye)



p-Aminoazobenzene
(yellow dye)

9.10 Importance of Diazonium Salts in Synthesis of Aromatic Compounds

From the above reactions, it is clear that the diazonium salts are very good intermediates for the introduction of –F, –Cl, –Br, –I, –CN, –OH, $-NO_2$ groups into the aromatic ring.

Aryl fluorides and iodides cannot be prepared by direct halogenation. The cyano group cannot be introduced by nucleophilic substitution of chlorine in chlorobenzene but cyanobenzene can be easily obtained from diazonium salt.

Thus, the replacement of diazo group by other groups is helpful in

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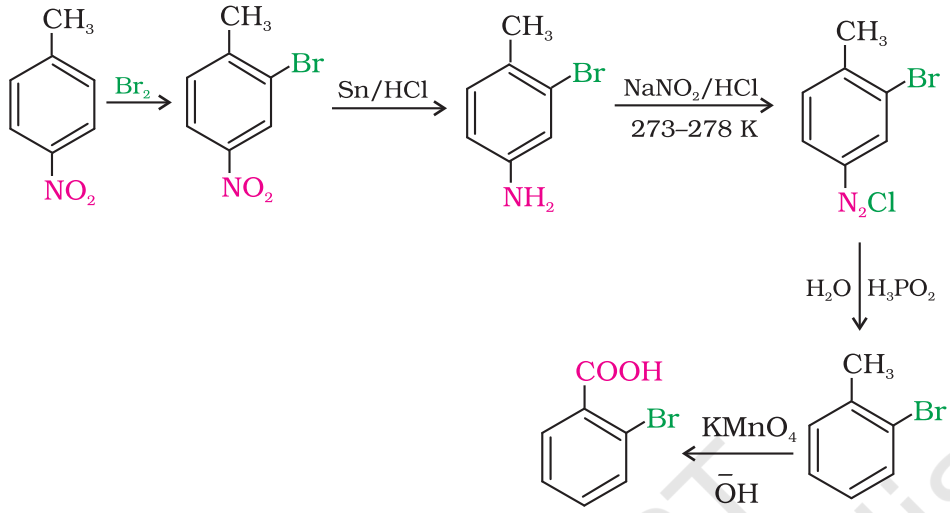
preparing those substituted aromatic compounds which cannot be prepared by direct substitution in benzene or substituted benzene.

Example 9.5

How will you convert 4-nitrotoluene to 2-bromobenzoic acid ?

Solution



Intext Question

9.9 Convert

(i) 3-Methylaniline into 3-nitrotoluene.

(ii) Aniline into 1,3,5 - tribromobenzene.

Summary

Amines can be considered as derivatives of ammonia obtained by replacement of hydrogen atoms with alkyl or aryl groups. Replacement of one hydrogen atom of ammonia gives rise to structure of the type **R-NH$_2$**, known as **primary amine**. **Secondary amines** are characterised by the structure **R$_2$NH** or **R-NHR′** and **tertiary amines** by **R$_3$N**, **RNR′R″** or **R$_2$NR′**. Secondary and tertiary amines are known as simple amines if the alkyl or aryl groups are the same and mixed amines if the groups are different. Like ammonia, all the three types of amines have one unshared electron pair on nitrogen atom due to which they behave as **Lewis bases**.

Amines are usually formed from nitro compounds, halides, amides, imides, etc. They exhibit hydrogen bonding which influence their physical properties. In **alkylamines**, a combination of electron releasing, steric and H-bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. Alkyl amines are found to be stronger bases than ammonia. In **aromatic amines**, electron releasing and withdrawing groups, respectively increase and decrease their basic character. **Aniline** is a weaker base

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than ammonia. Reactions of amines are governed by availability of the unshared pair of electrons on nitrogen. Influence of the number of hydrogen atoms at nitrogen atom on the type of reactions and nature of products is responsible for identification and distinction between primary, secondary and tertiary amines. *p*-Toluenesulphonyl chloride is used for the identification of primary, secondary and tertiary amines. Presence of amino group in aromatic ring enhances reactivity of the aromatic amines. Reactivity of aromatic amines can be controlled by **acylation** process, i.e., by treating with acetyl chloride or acetic anhydride. Tertiary amines like **trimethylamine** are used as insect attractants.

Aryldiazonium salts, usually obtained from arylamines, undergo replacement of the diazonium group with a variety of nucleophiles to provide advantageous methods for producing aryl halides, cyanides, phenols and arenes by reductive removal of the diazo group. Coupling reaction of aryldiazonium salts with phenols or arylamines give rise to the formation of **azo dyes**.

Exercises

9.1 Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.

(i) $(CH_3)_2CHNH_2$ (ii) $CH_3(CH_2)_2NH_2$ (iii) $CH_3NHCH(CH_3)_2$

(iv) $(CH_3)_3CNH_2$ (v) $C_6H_5NHCH_3$ (vi) $(CH_3CH_2)_2NCH_3$

(vii) *m*–$BrC_6H_4NH_2$

9.2 Give one chemical test to distinguish between the following pairs of compounds.

(i) Methylamine and dimethylamine (ii) Secondary and tertiary amines

(iii) Ethylamine and aniline (iv) Aniline and benzylamine

(v) Aniline and N-methylaniline.

9.3 Account for the following:

(i) pK_b of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not.

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

(iv) Although amino group is *o*– and *p*– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

9.4 Arrange the following:

(i) In decreasing order of the pK_b values:
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In increasing order of basic strength:
$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

(iii) In increasing order of basic strength:
(a) Aniline, *p*-nitroaniline and *p*-toluidine

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(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$.

(iv) In decreasing order of basic strength in gas phase:
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(v) In increasing order of boiling point:
C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

(vi) In increasing order of solubility in water:
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$.

9.5 How will you convert:

(i) Ethanoic acid into methanamine
(ii) Hexanenitrile into 1-aminopentane
(iii) Methanol to ethanoic acid
(iv) Ethanamine into methanamine
(v) Ethanoic acid into propanoic acid
(vi) Methanamine into ethanamine
(vii) Nitromethane into dimethylamine
(viii) Propanoic acid into ethanoic acid?

9.6 Describe a method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.

9.7 Write short notes on the following:

(i) Carbylamine reaction
(ii) Diazotisation
(iii) Hofmann's bromamide reaction
(iv) Coupling reaction
(v) Ammonolysis
(vi) Acetylation
(vii) Gabriel phthalimide synthesis.

9.8 Accomplish the following conversions:

(i) Nitrobenzene to benzoic acid
(ii) Benzene to *m*-bromophenol
(iii) Benzoic acid to aniline
(iv) Aniline to 2,4,6-tribromofluorobenzene
(v) Benzyl chloride to 2-phenylethanamine
(vi) Chlorobenzene to *p*-chloroaniline
(vii) Aniline to *p*-bromoaniline
(viii) Benzamide to toluene
(ix) Aniline to benzyl alcohol.

9.9 Give the structures of A, B and C in the following reactions:

(i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH+Br_2} C$

(ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(iii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0°C]{HNO_2} C$

(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\,K]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

(v) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

(vi) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\,K]{HNO_2} B \xrightarrow{C_6H_5OH} C$

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9.10 An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

9.11 Complete the following reactions:

(i) $C_6H_5NH_2 + CHCl_3 + \text{alc.KOH} \rightarrow$

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

(iii) $C_6H_5NH_2 + H_2SO_4\,(\text{conc.}) \rightarrow$

(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

(v) $C_6H_5NH_2 + Br_2\,(aq) \rightarrow$

(vi) $C_6H_5NH_2 + (CH_3CO)_2\,O \rightarrow$

(vii) $C_6H_5N_2Cl \xrightarrow[(ii)NaNO_2 / Cu, \Delta]{(i)HBF_4}$

9.12 Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

9.13 Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

9.14 Give plausible explanation for each of the following:

(i) Why are amines less acidic than alcohols of comparable molecular masses?

(ii) Why do primary amines have higher boiling point than tertiary amines?

(iii) Why are aliphatic amines stronger bases than aromatic amines?

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Answers to Some Intext Questions

9.4 (i) $C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

(ii) $C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$

(iii) $C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

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Unit 10

Biomolecules

Objectives

After studying this Unit, you will be able to

- explain the characteristics of biomolecules like carbohydrates, proteins and nucleic acids and hormones;
- classify carbohydrates, proteins, nucleic acids and vitamins on the basis of their structures;
- explain the difference between DNA and RNA;
- describe the role of biomolecules in biosystem.

"It is the harmonious and synchronous progress of chemical reactions in body which leads to life".

A living system grows, sustains and reproduces itself. The most amazing thing about a living system is that it is composed of non-living atoms and molecules. The pursuit of knowledge of what goes on chemically within a living system falls in the domain of ***biochemistry***. Living systems are made up of various complex biomolecules like carbohydrates, proteins, nucleic acids, lipids, etc. Proteins and carbohydrates are essential constituents of our food. These biomolecules interact with each other and constitute the molecular logic of life processes. In addition, some simple molecules like vitamins and mineral salts also play an important role in the functions of organisms. Structures and functions of some of these biomolecules are discussed in this Unit.

10.1 Carbohydrates

Carbohydrates are primarily produced by plants and form a very large group of naturally occurring organic compounds. Some common examples of carbohydrates are cane sugar, glucose, starch, etc. Most of them have a general formula, $C_x(H_2O)_y$, and were considered as hydrates of carbon from where the name carbohydrate was derived. For example, the molecular formula of glucose ($C_6H_{12}O_6$) fits into this general formula, $C_6(H_2O)_6$. But all the compounds which fit into this formula may not be classified as carbohydrates. For example acetic acid (CH_3COOH) fits into this general formula, $C_2(H_2O)_2$ but is not a carbohydrate. Similarly, rhamnose, $C_6H_{12}O_5$ is a carbohydrate but does not fit in this definition. A large number of their reactions have shown that they contain specific functional groups. Chemically, *the carbohydrates may be defined as optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis*. Some of the carbohydrates, which are sweet in taste, are also called sugars. The most common sugar, used in our homes is named as sucrose whereas the sugar present

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in milk is known as lactose. Carbohydrates are also called saccharides (Greek: *sakcharon* means sugar).

10.1.1 Classification of Carbohydrates

Carbohydrates are classified on the basis of their behaviour on hydrolysis. They have been broadly divided into following three groups.

(i) *Monosaccharides*: A carbohydrate that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone is called a monosaccharide. About 20 monosaccharides are known to occur in nature. Some common examples are glucose, fructose, ribose, etc.

(ii) *Oligosaccharides*: Carbohydrates that yield two to ten monosaccharide units, on hydrolysis, are called oligosaccharides. They are further classified as disaccharides, trisaccharides, tetrasaccharides, etc., depending upon the number of monosaccharides, they provide on hydrolysis. Amongst these the most common are disaccharides. The two monosaccharide units obtained on hydrolysis of a disaccharide may be same or different. For example, one molecule of sucrose on hydrolysis gives one molecule of glucose and one molecule of fructose whereas maltose gives two molecules of only glucose.

(iii) *Polysaccharides*: Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharides. Some common examples are starch, cellulose, glycogen, gums, etc. Polysaccharides are not sweet in taste, hence they are also called non-sugars.

The carbohydrates may also be classified as either reducing or non-reducing sugars. All those carbohydrates which reduce Fehling's solution and Tollens' reagent are referred to as reducing sugars. All monosaccharides whether aldose or ketose are *reducing sugars.*

10.1.2 Monosaccharides

Monosaccharides are further classified on the basis of number of carbon atoms and the functional group present in them. If a monosaccharide contains an aldehyde group, it is known as an aldose and if it contains a keto group, it is known as a ketose. Number of carbon atoms constituting the monosaccharide is also introduced in the name as is evident from the examples given in Table 10.1

Table 10.1: Different Types of Monosaccharides

Carbon atoms	General term	Aldehyde	Ketone
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose

10.1.2.1 Glucose

Glucose occurs freely in nature as well as in the combined form. It is present in sweet fruits and honey. Ripe grapes also contain glucose in large amounts. It is prepared as follows:

Preparation of Glucose

1. *From sucrose (Cane sugar)*: If sucrose is boiled with dilute HCl or H_2SO_4 in alcoholic solution, glucose and fructose are obtained in equal amounts.

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$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose — Glucose — Fructose

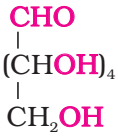
2. *From starch*: Commercially glucose is obtained by hydrolysis of starch by boiling it with dilute H_2SO_4 at 393 K under pressure.

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow[393K;\ 2\text{-}3\ atm]{H^+} nC_6H_{12}O_6$$

Starch or cellulose — Glucose

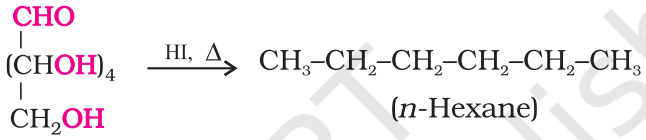
Structure of Glucose

Glucose is an aldohexose and is also known as dextrose. It is the monomer of many of the larger carbohydrates, namely starch, cellulose. It is probably the most abundant organic compound on earth. It was assigned the structure given below on the basis of the following evidences:



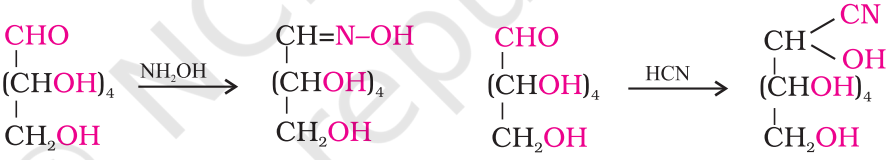
Glucose

1. Its molecular formula was found to be $C_6H_{12}O_6$.
2. On prolonged heating with HI, it forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain.

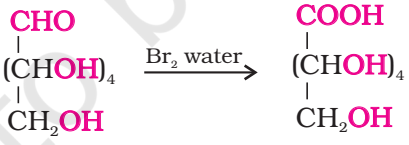


(n-Hexane)

3. Glucose reacts with hydroxylamine to form an oxime and adds a molecule of hydrogen cyanide to give cyanohydrin. These reactions confirm the presence of a carbonyl group (>C = O) in glucose.

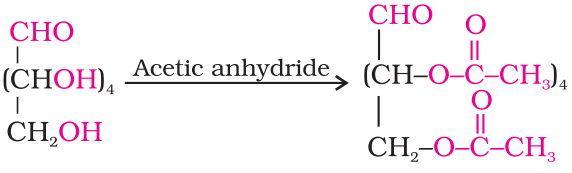


4. Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild oxidising agent like bromine water. This indicates that the carbonyl group is present as an aldehydic group.



Gluconic acid

5. Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five –OH groups. Since it exists as a stable compound, five –OH groups should be attached to different carbon atoms.



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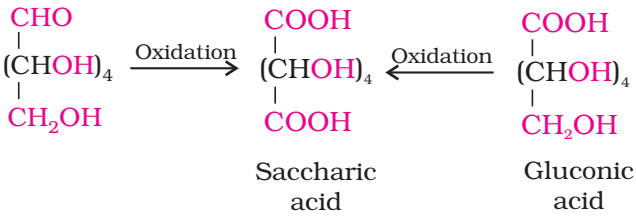
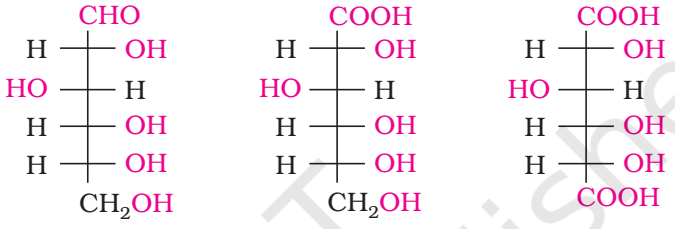
6. On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid. This indicates the presence of a primary alcoholic (–OH) group in glucose.



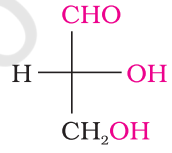
Saccharic acid | Gluconic acid

The exact spatial arrangement of different —OH groups was given by Fischer after studying many other properties. Its configuration is correctly represented as **I**. So gluconic acid is represented as **II** and saccharic acid as **III**.

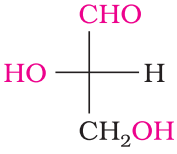


Glucose is correctly named as D(+)-glucose. 'D' before the name of glucose represents the configuration whereas '(+)' represents dextrorotatory nature of the molecule. It should be remembered that 'D' and 'L' have no relation with the optical activity of the compound. They are also not related to letter 'd' and 'l' (see Unit 6). The meaning of D– and L– notations is as follows.

The letters 'D' or 'L' before the name of any compound indicate the relative configuration of a particular stereoisomer of a compound with respect to configuration of some other compound, configuration of which is known. In the case of carbohydrates, this refers to their relation with a particular isomer of glyceraldehyde. Glyceraldehyde contains one asymmetric carbon atom and exists in two enantiomeric forms as shown below.



(+) – Glyceraldehyde



(–) – Glyceraldehyde

(+) Isomer of glyceraldehyde has 'D' configuration. It means that when its structural formula is written on paper following specific conventions which you will study in higher classes, the –OH group lies on right hand side in the structure. All those compounds which can be chemically correlated to D (+) isomer of glyceraldehyde are said to have D-configuration whereas those which can be correlated to 'L' (–) isomer of glyceraldehyde are said to have L—configuration. In L (–) isomer –OH group is on left hand side as you can see in the structure. For assigning

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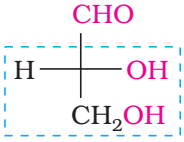
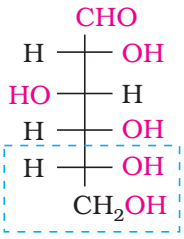
the configuration of monosaccharides, it is the lowest asymmetric carbon atom (as shown below) which is compared. As in (+) glucose, —OH on the lowest asymmetric carbon is on the right side which is comparable to (+) glyceraldehyde, so (+) glucose is assigned D-configuration. Other asymmetric carbon atoms of glucose are not considered for this comparison. Also, the structure of glucose and glyceraldehyde is written in a way that most oxidised carbon (in this case –CHO)is at the top.



D– (+) – Glyceraldehyde



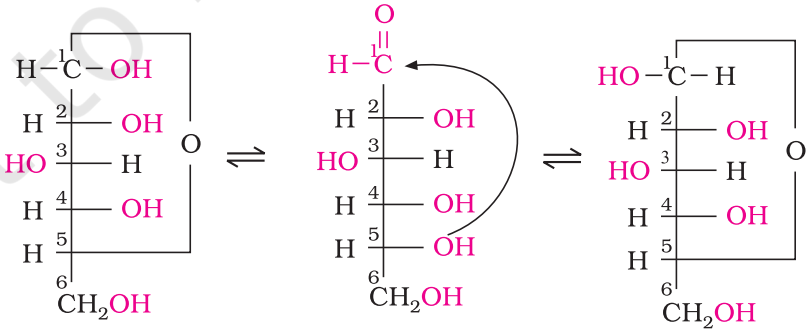
D–(+) – Glucose

Cyclic Structure of Glucose

The structure **(I)** of glucose explained most of its properties but the following reactions and facts could not be explained by this structure.

1. Despite having the aldehyde group, glucose does not give Schiff's test and it does not form the hydrogensulphite addition product with $NaHSO_3$.
2. The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free —CHO group.
3. Glucose is found to exist in two different crystalline forms which are named as α and β. The α-form of glucose (m.p. 419 K) is obtained by crystallisation from concentrated solution of glucose at 303 K while the β-form (m.p. 423 K) is obtained by crystallisation from hot and saturated aqueous solution at 371 K.

   This behaviour could not be explained by the open chain structure **(I)** for glucose. It was proposed that one of the —OH groups may add to the —CHO group and form a cyclic hemiacetal structure. It was found that glucose forms a six-membered ring in which —OH at C-5 is involved in ring formation. This explains the absence of —CHO group and also existence of glucose in two forms as shown below. These two cyclic forms exist in equilibrium with open chain structure.



α – D – (+) – Glucose

β – D– (+) – Glucose

The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called *anomeric carbon*

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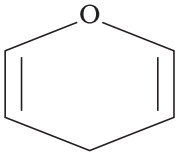
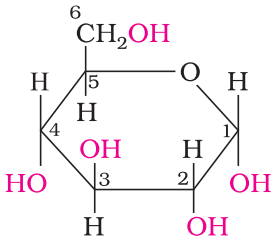
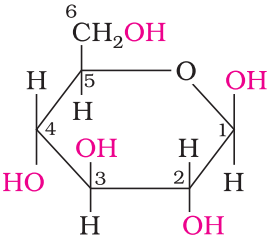
(the aldehyde carbon before cyclisation). Such isomers, i.e., α-form and β-form, are called **anomers**. The six membered cyclic structure of glucose is called **pyranose structure** (α– or β–), in analogy with pyran. Pyran is a cyclic organic compound with one oxygen atom and five carbon atoms in the ring. The cyclic structure of glucose is more correctly represented by Haworth structure as given below.



Pyran



α – D – (+) – Glucopyranose



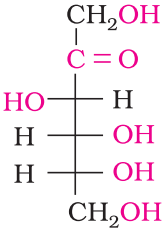
β – D – (+) – Glucopyranose

10.1.2.2 Fructose

Fructose is an important ketohexose. It is obtained along with glucose by the hydrolysis of disaccharide, sucrose. It is a natural monosaccharide found in fruits, honey and vegetables. In its pure form it is used as a sweetner. It is also an important ketohexose.

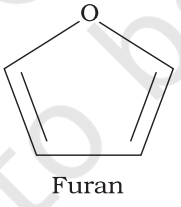
Structure of Fructose

Fructose also has the molecular formula $C_6H_{12}O_6$ and on the basis of its reactions it was found to contain a ketonic functional group at carbon number 2 and six carbons in straight chain as in the case of glucose. It belongs to D-series and is a laevorotatory compound. It is appropriately written as D-(–)-fructose. Its open chain structure is as shown.

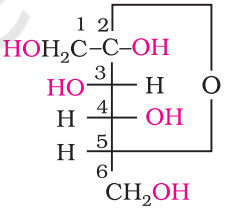


D – (–) – Fructose

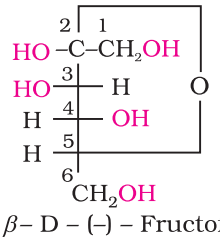
It also exists in two cyclic forms which are obtained by the addition of —OH at C5 to the (>C=O) group. The ring, thus formed is a five membered ring and is named as furanose with analogy to the compound furan. Furan is a five membered cyclic compound with one oxygen and four carbon atoms.



Furan

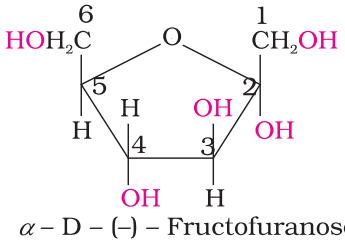


α – D – (–) – Fructofuranose

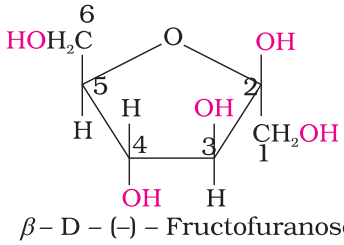


β – D – (–) – Fructofuranose

The cyclic structures of two anomers of fructose are represented by Haworth structures as given.



α – D – (–) – Fructofuranose



β – D – (–) – Fructofuranose

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10.1.3 Disaccharides

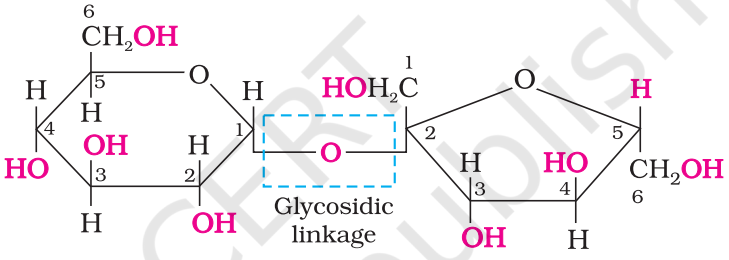
You have already read that disaccharides on hydrolysis with dilute acids or enzymes yield two molecules of either the same or different monosaccharides. The two monosaccharides are joined together by an oxide linkage formed by the loss of a water molecule. Such a linkage between two monosaccharide units through oxygen atom is called *glycosidic linkage.*

In disaccharides, if the reducing groups of monosaccharides i.e., aldehydic or ketonic groups are bonded, these are non-reducing sugars, e.g., sucrose. On the other hand, sugars in which these functional groups are free, are called reducing sugars, for example, maltose and lactose.

(i) Sucrose: One of the common disaccharides is **sucrose** which on hydrolysis gives equimolar mixture of D-(+)-glucose and D-(-) fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{D-(+)-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-(–)-Fructose}}{C_6H_{12}O_6}$$

These two monosaccharides are held together by a glycosidic linkage between C1 of α-D-glucose and C2 of β-D-fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non reducing sugar.

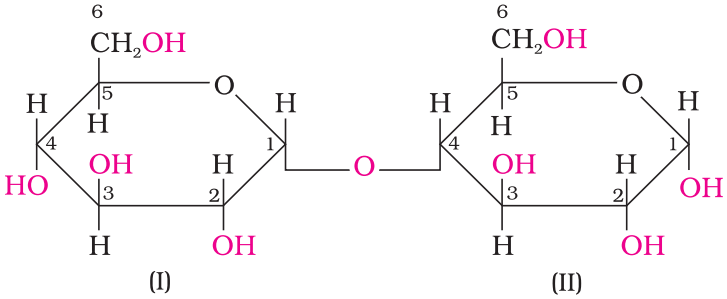


α – D – Glucose β – D – Fructose

Sucrose

Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+ 52.5°), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is named as **invert sugar**.

(ii) Maltose: Another disaccharide, maltose is composed of two α-D-glucose units in which C1 of one glucose (I) is linked to C4 of another glucose unit (II). The free aldehyde group can be produced at C1 of second glucose in solution and it shows reducing properties so it is a reducing sugar.



(I) α – D – Glucose (II) α – D – Glucose

Maltose

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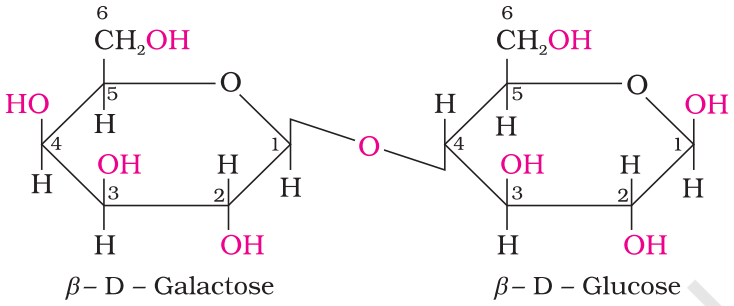
(iii) Lactose: It is more commonly known as milk sugar since this disaccharide is found in milk. It is composed of β-D-galactose and β-D-glucose. The linkage is between C1 of galactose and C4 of glucose. Free aldehyde group may be produced at C-1 of glucose unit, hence it is also a reducing sugar.



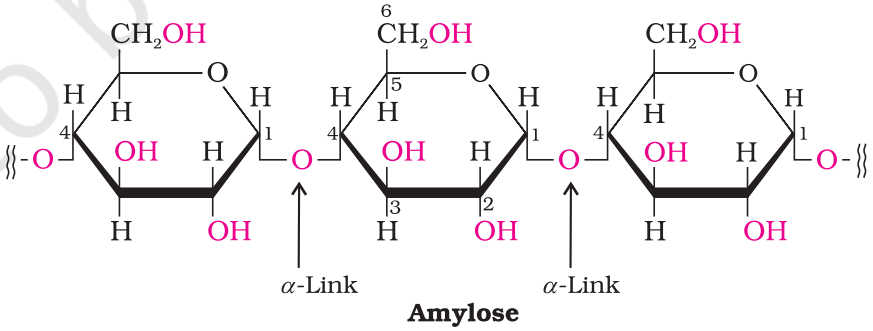
Lactose

10.1.4 Polysaccharides

Polysaccharides contain a large number of monosaccharide units joined together by glycosidic linkages. These are the most commonly encountered carbohydrates in nature. They mainly act as the food storage or structural materials.

(i) Starch: Starch is the main storage polysaccharide of plants. It is the most important dietary source for human beings. High content of starch is found in cereals, roots, tubers and some vegetables. It is a polymer of α-glucose and consists of two components—**Amylose** and **Amylopectin**. Amylose is water soluble component which constitutes about 15-20% of starch. Chemically amylose is a long unbranched chain with 200-1000 α-D-(+)-glucose units held together by C1– C4 glycosidic linkage.

Amylopectin is insoluble in water and constitutes about 80-85% of starch. It is a branched chain polymer of α-D-glucose units in which chain is formed by C1–C4 glycosidic linkage whereas branching occurs by C1–C6 glycosidic linkage.



Amylose

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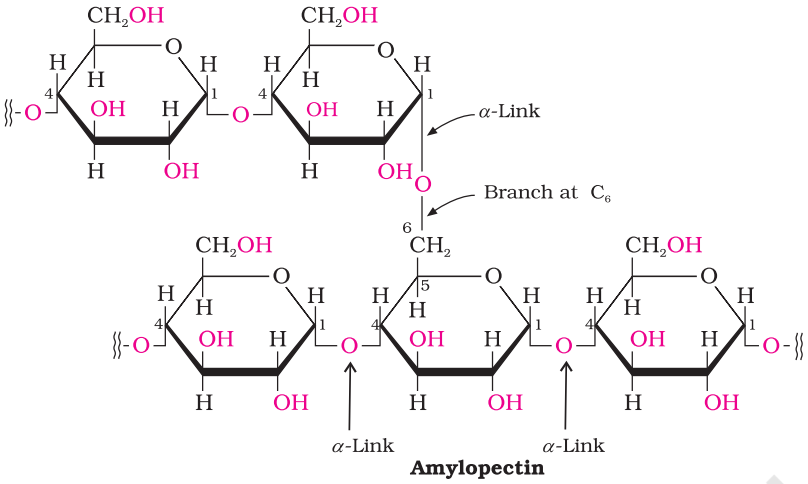
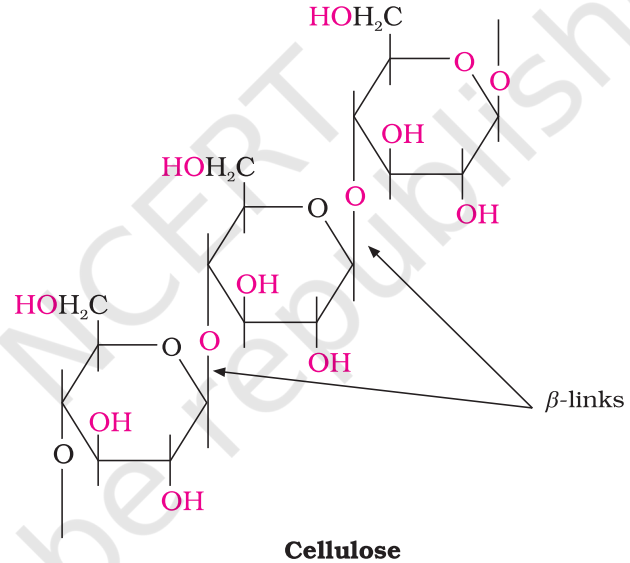


Amylopectin

(ii) Cellulose: Cellulose occurs exclusively in plants and it is the most abundant organic substance in plant kingdom. It is a predominant constituent of cell wall of plant cells. Cellulose is a straight chain



Cellulose

polysaccharide composed only of β-D-glucose units which are joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit.

(iii) Glycogen: The carbohydrates are stored in animal body as glycogen. It is also known as *animal starch* because its structure is similar to amylopectin and is rather more highly branched. It is present in liver, muscles and brain. When the body needs glucose, enzymes break the glycogen down to glucose. Glycogen is also found in yeast and fungi.

10.1.5 Importance of Carbohydrates

Carbohydrates are essential for life in both plants and animals. They form a major portion of our food. Honey has been used for a long time as an instant source of energy by '***Vaids***' in ayurvedic system of medicine. Carbohydrates are used as storage molecules as starch in plants and **glycogen** in animals. Cell wall of bacteria and plants is made up of cellulose. We build furniture, etc. from cellulose in the form

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of wood and clothe ourselves with cellulose in the form of cotton fibre. They provide raw materials for many important industries like textiles, paper, lacquers and breweries.

Two aldopentoses viz. D-ribose and 2-deoxy-D-ribose (Section 10.5.1, Class XII) are present in nucleic acids. Carbohydrates are found in biosystem in combination with many proteins and lipids.

Intext Questions

10.1 Glucose or sucrose are soluble in water but cyclohexane or benzene (simple six membered ring compounds) are insoluble in water. Explain.

10.2 What are the expected products of hydrolysis of lactose?

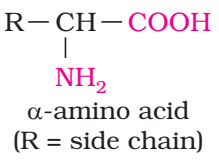
10.3 How do you explain the absence of aldehyde group in the pentaacetate of D-glucose?

10.2 Proteins

Proteins are the most abundant biomolecules of the living system. Chief sources of proteins are milk, cheese, pulses, peanuts, fish, meat, etc. They occur in every part of the body and form the fundamental basis of structure and functions of life. They are also required for growth and maintenance of body. The word protein is derived from Greek word, "**proteios**" which means primary or of prime importance. All proteins are polymers of α-amino acids.

10.2.1 Amino Acids

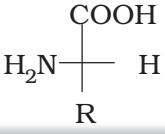
Amino acids contain amino ($-NH_2$) and carboxyl (–COOH) functional groups. Depending upon the relative position of amino group with respect to carboxyl group, the amino acids can be classified as α, β, γ, δ and so on. Only α-amino acids are obtained on hydrolysis of proteins. They may contain other functional groups also.



α-amino acid
(R = side chain)

All α-amino acids have trivial names, which usually reflect the property of that compound or its source. Glycine is so named since it has sweet taste (in Greek *glykos* means sweet) and tyrosine was first obtained from cheese (in Greek, *tyros* means cheese.) Amino acids are generally represented by a three letter symbol, sometimes one letter symbol is also used. Structures of some commonly occurring amino acids along with their 3-letter and 1-letter symbols are given in Table 10.2.

Table 10.2: Natural Amino Acids



Name of the amino acids	Characteristic feature of side chain, R	Three letter symbol	One letter code
1. Glycine	H	Gly	G
2. Alanine	$-CH_3$	Ala	A
3. Valine*	$(H_3C)_2CH-$	Val	V
4. Leucine*	$(H_3C)_2CH-CH_2-$	Leu	L

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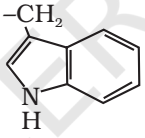
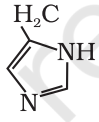
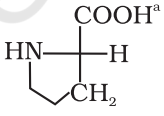
5. Isoleucine*	$H_3C\text{-}CH_2\text{-}CH(CH_3)\text{-}$	Ile	I
6. Arginine*	$HN{=}C(NH_2)\text{-}NH\text{-}(CH_2)_3\text{-}$	Arg	R
7. Lysine*	$H_2N\text{-}(CH_2)_4\text{-}$	Lys	K
8. Glutamic acid	$HOOC\text{-}CH_2\text{-}CH_2\text{-}$	Glu	E
9. Aspartic acid	$HOOC\text{-}CH_2\text{-}$	Asp	D
10. Glutamine	$H_2N\text{-}C(=O)\text{-}CH_2\text{-}CH_2\text{-}$	Gln	Q
11. Asparagine	$H_2N\text{-}C(=O)\text{-}CH_2\text{-}$	Asn	N
12. Threonine*	$H_3C\text{-}CHOH\text{-}$	Thr	T
13. Serine	$HO\text{-}CH_2\text{-}$	Ser	S
14. Cysteine	$HS\text{-}CH_2\text{-}$	Cys	C
15. Methionine*	$H_3C\text{-}S\text{-}CH_2\text{-}CH_2\text{-}$	Met	M
16. Phenylalanine*	$C_6H_5\text{-}CH_2\text{-}$	Phe	F
17. Tyrosine	$(p)HO\text{-}C_6H_4\text{-}CH_2\text{-}$	Tyr	Y
18. Tryptophan*		Trp	W
19. Histidine*		His	H
20. Proline		Pro	P

** essential amino acid, a = entire structure*

10.2.2 Classification of Amino Acids

Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule. Equal number of amino and carboxyl groups makes it neutral; more number of amino than carboxyl groups makes it basic and more carboxyl groups as compared to amino groups makes it acidic. The amino acids, which can be synthesised in the body, are known as **non-essential amino acids.** On the other hand, those which cannot be synthesised in the body and must be obtained through diet, are known as **essential amino acids** (marked with asterisk in Table 10.2).

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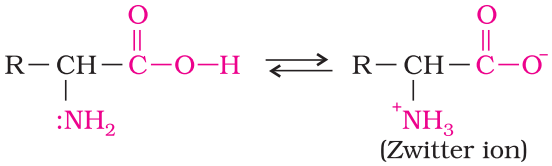
Amino acids are usually colourless, crystalline solids. These are water-soluble, high melting solids and behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule. In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as *zwitter ion*. This is neutral but contains both positive and negative charges.

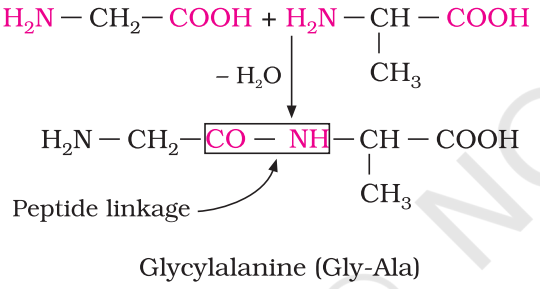


In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases.

Except glycine, all other naturally occurring α-amino acids are optically active, since the α-carbon atom is asymmetric. These exist both in 'D' and 'L' forms. Most naturally occurring amino acids have L-configuration. L-Aminoacids are represented by writing the $-NH_2$ group on left hand side.

10.2.3 Structure of Proteins

You have already read that proteins are the polymers of α-amino acids and they are connected to each other by **peptide bond** or **peptide linkage.** Chemically, peptide linkage is an amide formed between –COOH group and $-NH_2$ group. The reaction between two molecules of similar or different amino acids, proceeds through the combination of the amino group of one molecule with the carboxyl group of the other. This results in the elimination of a water molecule and formation of a peptide bond –CO–NH–. The product of the reaction is called a dipeptide because it is made up of two amino acids. For example, when carboxyl group of glycine combines with the amino group of alanine we get a **dipeptide**, glycylalanine.



If a third amino acid combines to a dipeptide, the product is called a **tripeptide**. A tripeptide contains three amino acids linked by two peptide linkages. Similarly when four, five or six amino acids are linked, the respective products are known as **tetrapeptide, pentapeptide or hexapeptide**, respectively. When the number of such amino acids is more than ten, then the products are called **polypeptides**. A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000u is called a protein. However, the distinction between a polypeptide and a protein is not very sharp. Polypeptides with fewer amino acids are likely to be called proteins if they ordinarily have a well defined conformation of a protein such as insulin which contains 51 amino acids.

Proteins can be classified into two types on the basis of their molecular shape.

(a) Fibrous proteins

When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre– like structure is formed. Such proteins are generally insoluble in water. Some common examples are keratin (present in hair, wool, silk) and myosin (present in muscles), etc.

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(b) Globular proteins

This structure results when the chains of polypeptides coil around to give a spherical shape. These are usually soluble in water. Insulin and albumins are the common examples of globular proteins.

Structure and shape of proteins can be studied at four different levels, i.e., primary, secondary, tertiary and quaternary, each level being more complex than the previous one.

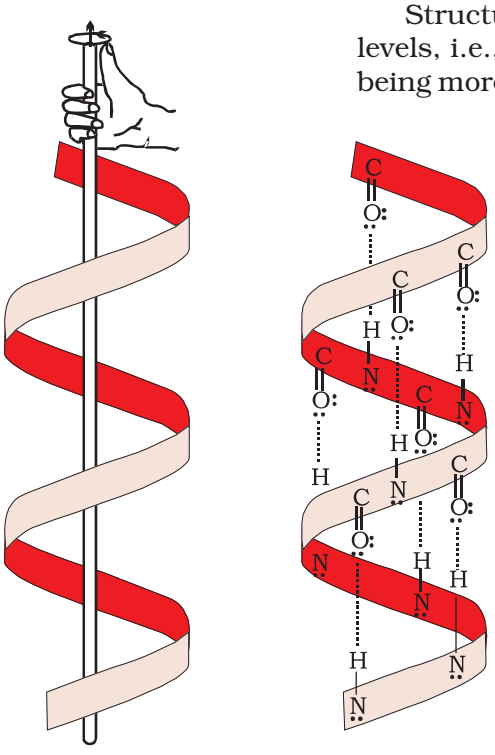

Fig. 10.1: α-Helix structure of proteins

(i) Primary structure of proteins: Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be the primary structure of that protein. Any change in this primary structure i.e., the sequence of amino acids creates a different protein.

(ii) Secondary structure of proteins: The secondary structure of protein refers to the shape in which a long polypeptide chain can exist. They are found to exist in two different types of structures viz. α-helix and β-pleated sheet structure. These structures arise due to the regular folding of the backbone of the polypeptide chain due to hydrogen bonding between $-\overset{\overset{O}{\|}}{C}-$ and –NH– groups of the peptide bond.

α-Helix is one of the most common ways in which a polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw (helix) with the $\diagup C{=}O$ group of each amino acid residue hydrogen bonded to the –NH of an adjacent turn of the helix as shown in Fig.10.1.

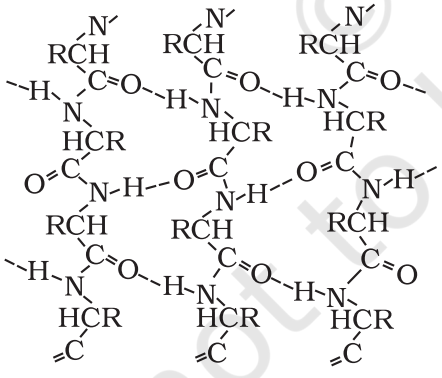

Fig. 10.2: β-Pleated sheet structure of proteins

In β-pleated sheet structure all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by intermolecular hydrogen bonds. The structure resembles the pleated folds of drapery and therefore is known as β-pleated sheet.

(iii) Tertiary structure of proteins: The tertiary structure of proteins represents overall folding of the polypeptide chains i.e., further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. The main forces which stabilise the 2° and 3° structures of proteins are hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.

(iv) Quaternary structure of proteins: Some of the proteins are composed of two or more polypeptide chains referred to as sub-units. The spatial arrangement of these subunits with respect to each other is known as quaternary structure.

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A diagrammatic representation of all these four structures is given in Figure 10.3 where each coloured ball represents an amino acid.

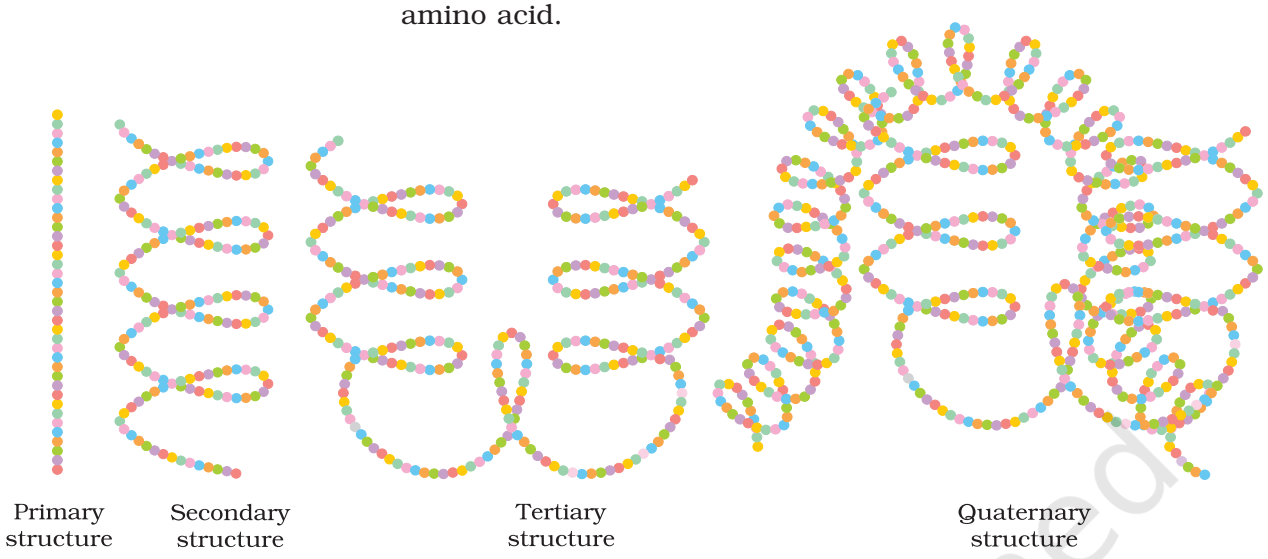

Fig. 10.3: *Diagrammatic representation of protein structure (two sub-units of two types in quaternary structure)*

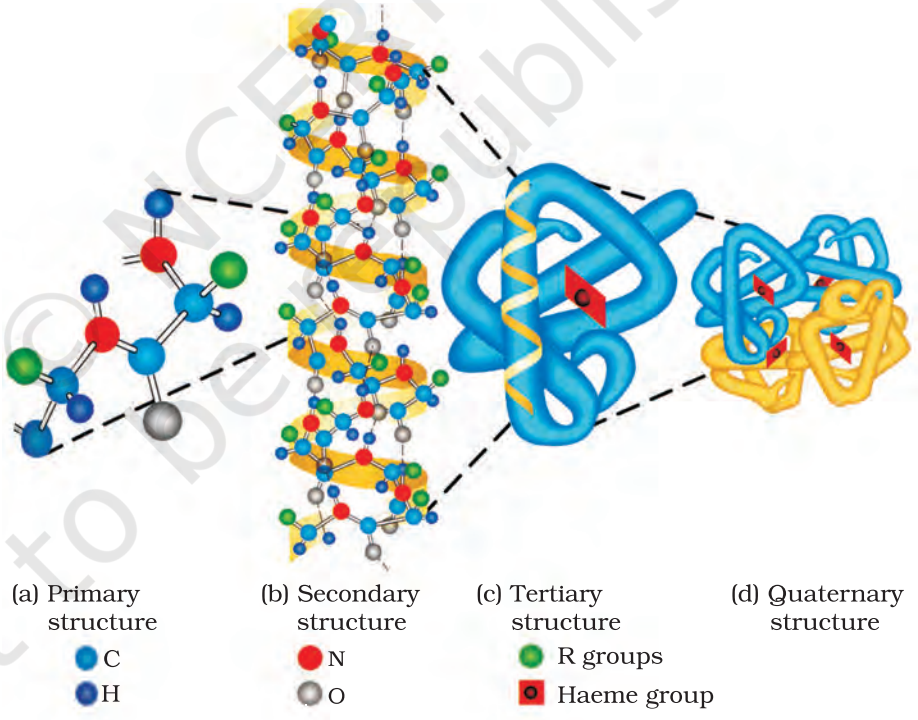

Fig. 10.4: *Primary, secondary, tertiary and quaternary structures of haemoglobin*

10.2.4 Denaturation of Proteins

Protein found in a biological system with a unique three-dimensional structure and biological activity is called a native protein. When a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called **denaturation** of

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protein. During denaturation secondary and tertiary structures are destroyed but primary structure remains intact. The coagulation of egg white on boiling is a common example of denaturation. Another example is curdling of milk which is caused due to the formation of lactic acid by the bacteria present in milk.

Intext Questions

10.4 The melting points and solubility in water of amino acids are generally higher than that of the corresponding halo acids. Explain.

10.5 Where does the water present in the egg go after boiling the egg?

10.3 Enzymes

Life is possible due to the coordination of various chemical reactions in living organisms. An example is the digestion of food, absorption of appropriate molecules and ultimately production of energy. This process involves a sequence of reactions and all these reactions occur in the body under very mild conditions. This occurs with the help of certain biocatalysts called **enzymes.** Almost all the enzymes are globular proteins. Enzymes are very specific for a particular reaction and for a particular substrate. They are generally named after the compound or class of compounds upon which they work. For example, the enzyme that catalyses hydrolysis of maltose into glucose is named as *maltase*.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Maltase}} 2\,\underset{\text{Glucose}}{C_6H_{12}O_6}$$

Sometimes enzymes are also named after the reaction, where they are used. For example, the enzymes which catalyse the oxidation of one substrate with simultaneous reduction of another substrate are named as **oxidoreductase** enzymes. The ending of the name of an enzyme is **-ase**.

10.3.1 Mechanism of Enzyme Action

Enzymes are needed only in small quantities for the progress of a reaction. Similar to the action of chemical catalysts, enzymes are said to reduce the magnitude of activation energy. For example, activation energy for acid hydrolysis of sucrose is 6.22 kJ mol^{-1}, while the activation energy is only 2.15 kJ mol^{-1} when hydrolysed by the enzyme, sucrase. Mechanism for the enzyme action has been discussed.

10.4 Vitamins

It has been observed that certain organic compounds are required in small amounts in our diet but their deficiency causes specific diseases. These compounds are called **vitamins.** Most of the vitamins cannot be synthesised in our body but plants can synthesise almost all of them, so they are considered as essential food factors. However, the bacteria of the gut can produce some of the vitamins required by us. All the vitamins are generally available in our diet. Different vitamins belong to various chemical classes and it is difficult to define them on the basis of structure. They are generally regarded as **organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth**

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and health of the organism. Vitamins are designated by alphabets A, B, C, D, etc. Some of them are further named as sub-groups e.g. B_1, B_2, B_6, B_{12}, etc. Excess of vitamins is also harmful and vitamin pills should not be taken without the advice of doctor.

The term "**Vitamine**" was coined from the word vital + amine since the earlier identified compounds had amino groups. Later work showed that most of them did not contain amino groups, so the letter 'e' was dropped and the term **vitamin** is used these days.

10.4.1 Classification of Vitamins

Vitamins are classified into two groups depending upon their solubility in water or fat.

(i) *Fat soluble vitamins*: Vitamins which are soluble in fat and oils but insoluble in water are kept in this group. These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues.

(ii) *Water soluble vitamins*: B group vitamins and vitamin C are soluble in water so they are grouped together. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot be stored (except vitamin B_{12}) in our body.

Some important vitamins, their sources and diseases caused by their deficiency are listed in Table 10.3.

Table 10.3: Some important Vitamins, their Sources and their Deficiency Diseases

Sl. No.	Name of Vitamins	Sources	Deficiency diseases
1.	Vitamin A	Fish liver oil, carrots, butter and milk	Xerophthalmia (hardening of cornea of eye) Night blindness
2.	Vitamin B_1 (Thiamine)	Yeast, milk, green vegetables and cereals	Beri beri (loss of appetite, retarded growth)
3.	Vitamin B_2 (Riboflavin)	Milk, eggwhite, liver, kidney	Cheilosis (fissuring at corners of mouth and lips), digestive disorders and burning sensation of the skin.
4.	Vitamin B_6 (Pyridoxine)	Yeast, milk, egg yolk, cereals and grams	Convulsions
5.	Vitamin B_{12}	Meat, fish, egg and curd	Pernicious anaemia (RBC deficient in haemoglobin)
6.	Vitamin C (Ascorbic acid)	Citrus fruits, amla and green leafy vegetables	Scurvy (bleeding gums)
7.	Vitamin D	Exposure to sunlight, fish and egg yolk	Rickets (bone deformities in children) and osteomalacia (soft bones and joint pain in adults)

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8. Vitamin E	Vegetable oils like wheat germ oil, sunflower oil, etc.	Increased fragility of RBCs and muscular weakness
9. Vitamin K	Green leafy vegetables	Increased blood clotting time

10.5 Nucleic Acids

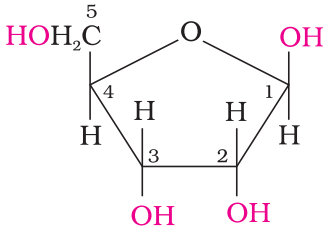
Every generation of each and every species resembles its ancestors in many ways. How are these characteristics transmitted from one generation to the next? It has been observed that nucleus of a living cell is responsible for this transmission of inherent characters, also called **heredity**. The particles in nucleus of the cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called **nucleic acids.** These are mainly of two types, the **deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).** Since nucleic acids are long chain polymers of **nucleotides,** so they are also called polynucleotides.

James Dewey Watson

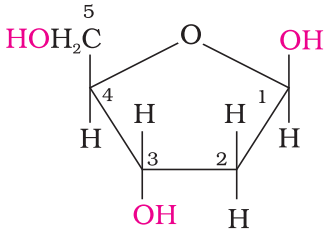
Born in Chicago, Illinois, in 1928, Dr Watson received his Ph.D. (1950) from Indiana University in Zoology. He is best known for his discovery of the structure of DNA for which he shared with Francis Crick and Maurice Wilkins the 1962 Nobel prize in Physiology and Medicine. They proposed that DNA molecule takes the shape of a double helix, an elegantly simple structure that resembles a gently twisted ladder. The rails of the ladder are made of alternating units of phosphate and the sugar deoxyribose; the rungs are each composed of a pair of purine/ pyrimidine bases. This research laid the foundation for the emerging field of **molecular biology**. The complementary pairing of nucleotide bases explains how identical copies of parental DNA pass on to two daughter cells. This research launched a revolution in biology that led to modern recombinant DNA techniques.

10.5.1 Chemical Composition of Nucleic Acids

Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds (called bases). In DNA molecules, the sugar moiety is β-D-2-deoxyribose whereas in RNA molecule, it is β-D-ribose.



β–D–ribose



β–D–2–deoxyribose

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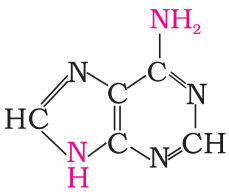
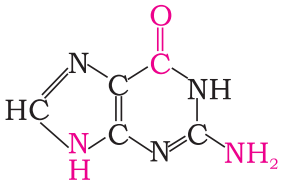
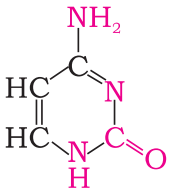
DNA contains four bases viz. adenine (A), guanine (G), cytosine (C) and thymine (T). RNA also contains four bases, the first three bases are same as in DNA but the fourth one is uracil (U).



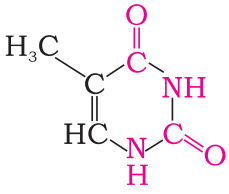
Adenine (A)



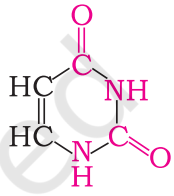
Guanine (G)



Cytosine (C)



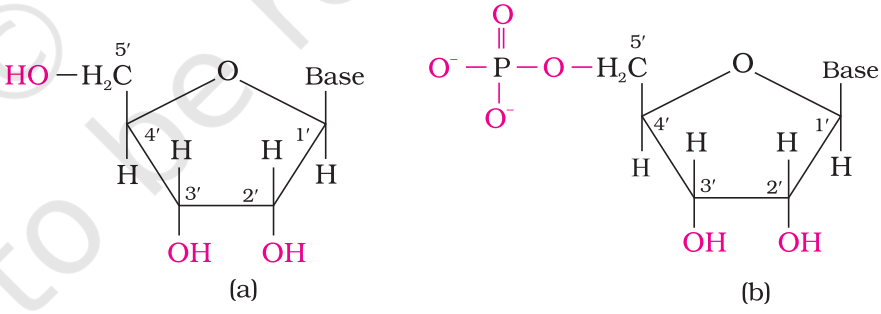
Thymine (T)



Uracil (U)

10.5.2 Structure of Nucleic Acids

A unit formed by the attachment of a base to 1′ position of sugar is known as **nucleoside.** In nucleosides, the sugar carbons are numbered as 1′, 2′, 3′, etc. in order to distinguish these from the bases (Fig. 10.5a). When nucleoside is linked to phosphoric acid at 5′-position of sugar moiety, we get a nucleotide (Fig. 10.5).



(a) (b)

Fig. 10.5: *Structure of (a) a nucleoside and (b) a nucleotide*

Nucleotides are joined together by phosphodiester linkage between 5′ and 3′ carbon atoms of the pentose sugar. The formation of a typical dinucleotide is shown in Fig. 10.6.

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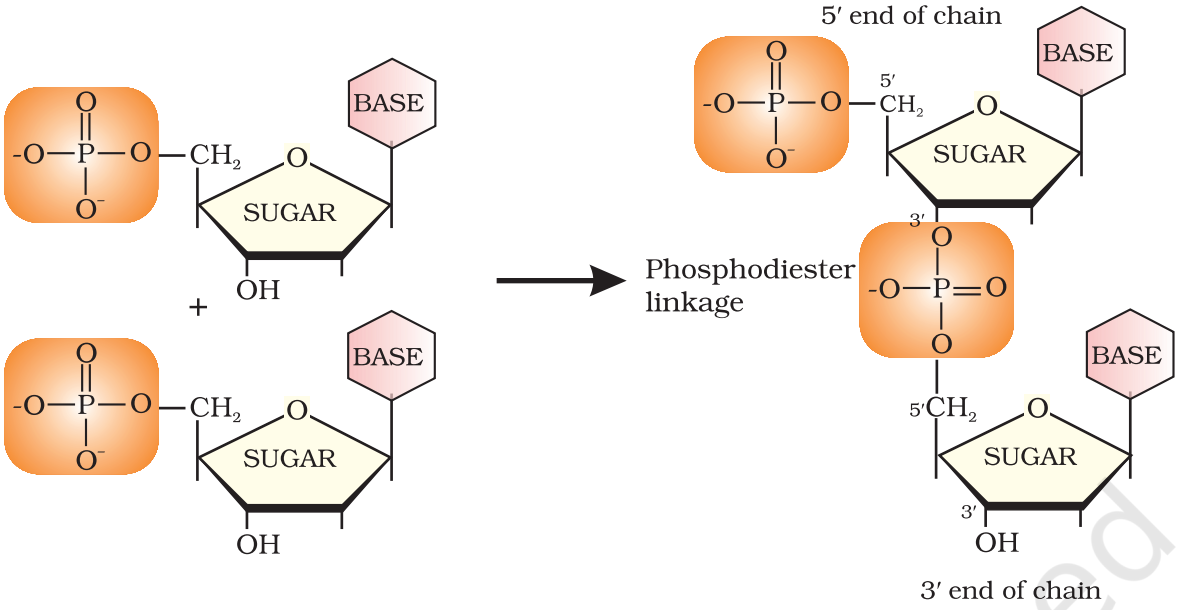
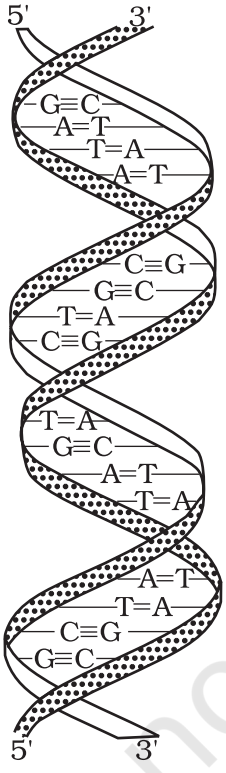


Fig. 10.6: Formation of a dinucleotide



A simplified version of nucleic acid chain is as shown below.

Base — Sugar — Phosphate — (Base — Sugar — Phosphate)$_n$ — Base — Sugar

Information regarding the sequence of nucleotides in the chain of a nucleic acid is called its primary structure. Nucleic acids have a secondary structure also. James Watson and Francis Crick gave a double strand helix structure for DNA (Fig. 10.7). Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.

In secondary structure of RNA single stranded helics is present which sometimes foldsback on itself. RNA molecules are of three types and they perform different functions. They are named as **messenger RNA (m-RNA), ribosomal RNA (r-RNA) and transfer RNA (t-RNA).**

Fig. 10.7: Double strand helix structure for DNA

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Har Gobind Khorana

Har Gobind Khorana, was born in 1922. He obtained his M.Sc. degree from Punjab University in Lahore. He worked with Professor Vladimir Prelog, who moulded Khorana's thought and philosophy towards science, work and effort. After a brief stay in India in 1949, Khorana went back to England and worked with Professor G.W. Kenner and Professor A.R.Todd. It was at Cambridge, U.K. that he got interested in both proteins and nucleic acids. Dr Khorana shared the Nobel Prize for Medicine and Physiology in 1968 with Marshall Nirenberg and Robert Holley for cracking the genetic code.

DNA Fingerprinting

It is known that every individual has unique fingerprints. These occur at the tips of the fingers and have been used for identification for a long time but these can be altered by surgery. A sequence of bases on DNA is also unique for a person and information regarding this is called DNA fingerprinting. It is same for every cell and cannot be altered by any known treatment. DNA fingerprinting is now used

(i) in forensic laboratories for identification of criminals.

(ii) to determine paternity of an individual.

(iii) to identify the dead bodies in any accident by comparing the DNA's of parents or children.

(iv) to identify racial groups to rewrite biological evolution.

10.5.3 Biological Functions of Nucleic Acids

DNA is the chemical basis of heredity and may be regarded as the reserve of genetic information. DNA is exclusively responsible for maintaining the identity of different species of organisms over millions of years. A DNA molecule is capable of self duplication during cell division and identical DNA strands are transferred to daughter cells. Another important function of nucleic acids is the protein synthesis in the cell. Actually, the proteins are synthesised by various RNA molecules in the cell but the message for the synthesis of a particular protein is present in DNA.

10.6 Hormones

Hormones are molecules that act as intercellular messengers. These are produced by endocrine glands in the body and are poured directly in the blood stream which transports them to the site of action.

In terms of chemical nature, some of these are steroids, e.g., estrogens and androgens; some are poly peptides for example insulin and endorphins and some others are amino acid derivatives such as epinephrine and norepinephrine.

Hormones have several functions in the body. They help to maintain the balance of biological activities in the body. The role of insulin in keeping the blood glucose level within the narrow limit is an example of this function. Insulin is released in response to the rapid rise in blood glucose level. On the other hand hormone glucagon tends to increase the glucose level in the blood. The two hormones together regulate the glucose level in the blood. Epinephrine and norepinephrine mediate responses to external stimuli. Growth hormones and sex hormones play role in growth and development. Thyroxine produced in the thyroid gland is an iodinated derivative of amino acid tyrosine. Abnormally low level of thyroxine leads

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to hypothyroidism which is characterised by lethargyness and obesity. Increased level of thyroxine causes hyperthyroidism. Low level of iodine in the diet may lead to hypothyroidism and enlargement of the thyroid gland. This condition is largely being controlled by adding sodium iodide to commercial table salt ("Iodised" salt).

Steroid hormones are produced by adrenal cortex and gonads (testes in males and ovaries in females). Hormones released by the adrenal cortex play very important role in the functions of the body. For example, glucocorticoids control the carbohydrate metabolism, modulate inflammatory reactions, and are involved in reactions to stress. The mineralocorticoids control the level of excretion of water and salt by the kidney. If adrenal cortex does not function properly then one of the results may be Addison's disease characterised by hypoglycemia, weakness and increased susceptibility to stress. The disease is fatal unless it is treated by glucocorticoids and mineralocorticoids. Hormones released by gonads are responsible for development of secondary sex characters. Testosterone is the major sex hormone produced in males. It is responsible for development of secondary male characteristics (deep voice, facial hair, general physical constitution) and estradiol is the main female sex hormone. It is responsible for development of secondary female characteristics and participates in the control of menstrual cycle. Progesterone is responsible for preparing the uterus for implantation of fertilised egg.

Intext Questions

10.6 Why cannot vitamin C be stored in our body?

10.7 What products would be formed when a nucleotide from DNA containing thymine is hydrolysed?

10.8 When RNA is hydrolysed, there is no relationship among the quantities of different bases obtained. What does this fact suggest about the structure of RNA?

Summary

Carbohydrates are optically active polyhydroxy aldehydes or ketones or molecules which provide such units on hydrolysis. They are broadly classified into three groups — **monosaccharides**, **disaccharides** and **polysaccharides**. Glucose, the most important source of energy for mammals, is obtained by the digestion of starch. Monosaccharides are held together by glycosidic linkages to form disaccharides or polysaccharides.

Proteins are the **polymers** of about twenty different **α-amino acids** which are linked by peptide bonds. Ten amino acids are called essential amino acids because they cannot be synthesised by our body, hence must be provided through diet. Proteins perform various structural and dynamic functions in the organisms. Proteins which contain only α-amino acids are called simple proteins. The **secondary** or **tertiary structure of proteins** get disturbed on change of pH or temperature and they are not able to perform their functions. This is called **denaturation of proteins**. Enzymes are **biocatalysts** which speed up the reactions in biosystems. They are very specific and selective in their action and chemically majority of **enzymes** are proteins.

Vitamins are accessory food factors required in the diet. They are classified as fat soluble (A, D, E and K) and water soluble (B group and C). Deficiency of vitamins leads to many diseases.

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Nucleic acids are the polymers of nucleotides which in turn consist of a base, a pentose sugar and phosphate moiety. Nucleic acids are responsible for the transfer of characters from parents to offsprings. There are two types of nucleic acids — **DNA** and **RNA**. DNA contains a five carbon sugar molecule called **2-deoxyribose** whereas RNA contains ribose. Both DNA and RNA contain adenine, guanine and cytosine. The fourth base is thymine in DNA and uracil in RNA. The structure of DNA is a double strand whereas RNA is a single strand molecule. DNA is the chemical basis of heredity and have the coded message for proteins to be synthesised in the cell. There are three types of RNA — mRNA, rRNA and tRNA which actually carry out the protein synthesis in the cell.

Exercises

10.1 What are monosaccharides?

10.2 What are reducing sugars?

10.3 Write two main functions of carbohydrates in plants.

10.4 Classify the following into monosaccharides and disaccharides.
Ribose, 2-deoxyribose, maltose, galactose, fructose and lactose.

10.5 What do you understand by the term glycosidic linkage?

10.6 What is glycogen? How is it different from starch?

10.7 What are the hydrolysis products of
(i) sucrose and (ii) lactose?

10.8 What is the basic structural difference between starch and cellulose?

10.9 What happens when D-glucose is treated with the following reagents?
(i) HI (ii) Bromine water (iii) HNO_3

10.10 Enumerate the reactions of D-glucose which cannot be explained by its open chain structure.

10.11 What are essential and non-essential amino acids? Give two examples of each type.

10.12 Define the following as related to proteins
(i) Peptide linkage (ii) Primary structure (iii) Denaturation.

10.13 What are the common types of secondary structure of proteins?

10.14 What type of bonding helps in stabilising the α-helix structure of proteins?

10.15 Differentiate between globular and fibrous proteins.

10.16 How do you explain the amphoteric behaviour of amino acids?

10.17 What are enzymes?

10.18 What is the effect of denaturation on the structure of proteins?

10.19 How are vitamins classified? Name the vitamin responsible for the coagulation of blood.

10.20 Why are vitamin A and vitamin C essential to us? Give their important sources.

10.21 What are nucleic acids? Mention their two important functions.

10.22 What is the difference between a nucleoside and a nucleotide?

10.23 The two strands in DNA are not identical but are complementary. Explain.

10.24 Write the important structural and functional differences between DNA and RNA.

10.25 What are the different types of RNA found in the cell?

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